

DEPARTMENT OF MECHANICAL ENGINEERING AND MECHANICS  
SCHOOL OF ENGINEERING  
OLD DOMINION UNIVERSITY  
NORFOLK, VIRGINIA

SURFACE-SLIP EQUATIONS FOR MULTICOMPONENT,  
NONEQUILIBRIUM AIR FLOW

By

Roop N. Gupta,

Carl D. Scott,

and

James N. Moss

Gene Goglia, Principal Investigator

Final Report

For the period ending September 30, 1984

Prepared for the  
National Aeronautics and Space Administration  
Langley Research Center  
Hampton, Virginia 23665

Under

Research Grant NAG-1-346

Ernest V. Zoby, Technical Monitor  
SSD-Aerothermodynamics Branch

April 1985

(NASA-CR-181252) SURFACE-SLIP EQUATIONS FOR  
MULTICOMPONENT, NONEQUILIBRIUM AIR FLOW

Final Report, period ending 30 Sep. 1984

(Old Dominion Univ.) 97 p Avail: NTIS HC

AC5/MF A01

CSCL 20D G3/34

N87-27945

Unclas  
0093174

P.97

Langley  
Grant

11-31-84

93174

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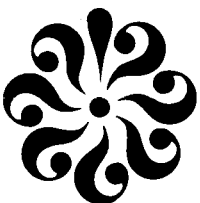
Research Grant NAG-1-246

Ernest V. Zoby, Technical Monitor

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Submitted by the  
Old Dominion University Research Foundation  
P. O. Box 6369  
Norfolk, Virginia 23508

April 1985



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# NOMENCLATURE

$A_k^i, B_{kl}^i, C_k^{i(j)}$	Coefficients of the velocity distribution function for $i$ th species
$a_{i0}, a_{i1}, b_{i0}, c_{i0}^{(j)}$	Distribution function coefficients defined in ref. 5 for $i$ th species
$a_\infty$	Speed of sound, $\sqrt{\gamma R T_\infty}$
$C_i$	Mass fraction of species $i$
$C_{pi}$	Specific heat at constant pressure of species $i$
$C_p$	Frozen specific heat at constant pressure of the mixture, $\sum_{i=1}^{NS} C_i C_{pi}$
$D_{ij}$	Multicomponent diffusion coefficient for species pair " $i$ " and " $j$ "
$D_{ij}$	Binary diffusion coefficient
$D_i^T$	Thermal diffusion coefficient
$d_k^j$	Diffusion vector of $j$ th species
$E$	Total energy flux, $E^T + eM$
$E^T$	Energy flux from translational energy
$e$	Internal energy that readily equilibrates with translational energy
$F$	General flux of property such as mass, momentum, or energy
$f^i$	Distribution function of $i$ th species
$f^{(0)i}$	Equilibrium (or Maxwellian) distribution function of $i$ th species
$h$	Enthalpy, $\sum_{i=1}^{NS} h_i C_i$
$h_i$	Enthalpy of species $i$
$K$	Thermal conductivity of mixture
$k$	Boltzmann constant

$k_{wi}$	Wall catalytic recombination rate constant for species $i$
$L_{ij}$	Multicomponent Lewis number, $C_p \rho D_{ij}/K$
$\bar{L}_{ij}$	Binary Lewis number, $C_p \rho D_{ij}/K$
$Le$	Binary Lewis number, $C_p \rho D_{AM}/K$
$M$	Mass flux
$M_\infty$	Mach number, $U_\infty/a_\infty$
$m_i$	Mass of $i$ th species
$\bar{m}$	Mass of a mixture molecule
$NS$	Number of chemical species
$n_i$	Number density of species $i$
$\bar{n}$	Total number density
$n^*$	Coordinate measured normal to the body in the body-filled coordinate system (Appendices C and D)
$Pr$	Prandtl number, $C_p \mu/K$
$P$	Momentum flux
$p$	Pressure
$p_i$	Partial pressure of species $i$
$q_w$	Wall heat-transfer rate
$R$	Gas constant
$R^*$	Radius measured from axis of symmetry to a point on the body surface
$Re$	Reynolds number, $\rho_\infty U_\infty r_N/\mu_{ref}$
$R$	Universal gas constant
$r$	Radial distance from body center (Appendix E)
$r_N$	Body nose radius of curvature (Appendix D) or radius of sphere (Appendix E)
$s^*$	Distance measured along the body surface (Appendix D)

$T$	Temperature
$U_{\infty}$	Free stream velocity
$u$	Velocity component along the body surface (Appendices C and D)
$v_k^i$	Thermal (or peculiar, or molecular) velocity of the $i$ th species
$\bar{v}_k^i$	Diffusion velocity
$v_{ok}$	Bulk or mass averaged velocity
$w_{ok}$	Nondimensional mass averaged velocity, $\sqrt{\frac{m_i}{2KT}} v_{ok}$
$w_k^i$	Nondimensional thermal velocity, $\sqrt{\frac{m_i}{2kT}} v_k^i$
$w_i$	Molecular (or atomic) weight of species $i$
$\bar{w}$	Molecular weight of mixture
$x$	Coordinate parallel to body (Fig. 1)
$y$	Coordinate perpendicular to body (Fig. 1).
$z$	Coordinate parallel to body (Fig. 1)
$\alpha$	Energy accommodation coefficient
$\beta$	Body angle defined in Fig. D1
$\delta_{kl}$	Kronecker delta
$\epsilon$	Reynolds number parameter, $[\mu_{ref}/\rho_{\infty} U_{\infty} r_N]^{1/2}$
$\gamma_i$	Recombination coefficient (or, fraction of incident atoms that recombine at surface)
$\bar{\gamma}$	Ratio of specific heats
$\kappa$	Surface curvature
$\lambda$	Mean free path
$\mu$	Viscosity of mixture
$\phi$	Perturbation part of distribution function
$\phi^i(\vec{V})$	General property of $i$ th species such as mass, momentum and energy

$\phi$	Circumferential angle (Appendices D and E)
$\rho$	Density
$\theta, \theta_i$	Accommodation coefficient (or fraction of incident particles that stick)

Affixes (Used both as subscripts and superscripts)

$i, j$	Species indices
$s$	Edge of Knudsen layer
$w$	Wall

Subscripts

$A$	Atom
$e$	Equilibrium value
$M$	Molecule
$i, j$	Specie indices
$k, l$	Coordinate indices
$q$	Specie index
$ref$	Reference quantity
$x, y, z$	Component directions
$y$	Normal component
$  , y, z$	Tangential components
$\infty$	Freestream value

Superscripts

$-$	Dimensionless quantity; also used locally
$\downarrow$	Incident flux
$\uparrow$	Specularly reflected flux



# SURFACE-SLIP EQUATIONS FOR MULTICOMPONENT, NONEQUILIBRIUM AIR FLOW\*

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## SUMMARY

Equations are presented for the surface slip (or jump) values of species concentration, pressure, velocity, and temperature in the low-Reynolds-number, high-altitude flight regime of a space vehicle. These are obtained from closed-form solutions of the mass, momentum, and energy flux equations using the Chapman-Enskog velocity distribution function. This function represents a solution of the Boltzmann equation in the Navier-Stokes approximation. The analysis, obtained for nonequilibrium multicomponent air flow, includes the finite-rate surface catalytic recombination and changes in the internal energy during reflection from the surface. Expressions for the various slip quantities have been obtained in a form which can readily be employed in flow-field computations. A consistent set of equations is provided for multicomponent, binary, and single species mixtures. Expression is also provided for the finite-rate species-concentration boundary condition for a multicomponent mixture in absence of slip.

## INTRODUCTION

For an accurate prediction of the aerothermal environment of a space vehicle entering the earth's atmosphere in the high-altitude low-Reynolds-number flight regime (Ref. 1), the multicomponent, nonequilibrium gas chemistry as well as the wall slip and catalysis effects, must be evaluated.

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\*The authors are grateful to Dr. Fred G. Blottner (of Sandia National Laboratories, Albuquerque, NM) for many useful discussions pertaining to the mass flux expressions contained in Appendix B.

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Such flow fields are of particular interest for aeroassist and space shuttle vehicles. This study was undertaken to obtain the boundary relations that incorporate the effects of slip, multicomponent diffusion, wall catalycity, and changes in internal energy of the molecules (during reflection from the surface) for application to flow-field calculations under the general assumption of local thermodynamic equilibrium.

Scott (Ref. 2) first presented the wall boundary conditions for a multicomponent mixture with diffusion and wall-catalysed atom recombination. In obtaining these boundary conditions, he used a first order velocity distribution function at the edge of the Knudsen layer next to the wall, where the continuum model of the gas breaks down. These boundary conditions, obtained from the kinetic theory considerations, provide solutions at the top of the Knudsen layer that would match the solution of the Navier-Stokes equations in the bulk outer flow. Hendricks (Ref. 3), using Scott's formulation, obtained simplified expressions for engineering applications with some corrections to Scott's expressions. Hendricks' analysis, however, contained some gross errors in obtaining the engineering expressions. This paper reanalyses the wall boundary equations by using the approach of reference 2 and provides appropriate relations for the various quantities with surface slip in a form which can readily be employed for flow-field computations. An effort has also been made to reconcile the differences between slip expressions employed by the different researchers. The present analysis provides a consistent formulation for the slip equations for a multicomponent, binary, and single species mixture. Expression is also provided for the finite-rate species-concentration boundary condition for a multicomponent mixture (in addition to that for a binary mixture) in the absence of slip. This may be of interest for the shuttle flow-field calculations based on multicomponent diffusion (Ref. 4).

The main difference (among other details) between the results contained in reference 5 and the present work is that the various internal degrees of freedom for a molecule were considered frozen during reflection from the surface in reference 5, whereas, they are allowed to change in the present analysis.\*\*\* Further, the results are provided in both spherical and body-oriented coordinate system.

### ANALYSIS

The slip conditions are taken to exist across the Knudsen layer, which is on the order of one mean free path in thickness as sketched in Figure 1. The analysis outlined here follows the approach of References 2 and 5. It is based on Shidlovskiy's (Ref. 6) assumption that the distribution function near the wall can be described to first-order accuracy by the so-called Navier-Stokes approximation. However, a deviation is made from the procedures of Shidlovskiy in that a Chapman-Enskog type distribution function for a multicomponent mixture obtained by the variational method of Hirschfelder, Curtiss, and Bird (Ref. 7) is used. The Chapman-Enskog distribution function allows accounting for diffusion. The analysis contains the following assumptions:

- (i) The energy and momentum accommodation coefficients (i.e.  $\alpha$  and  $\theta$ , respectively) have the same value.
- (ii) The fluxes of mass, momentum, and energy across the Knudsen layer are assumed constant. This is consistent with the assumption of negligible variation of the velocity distribution function through the Knudsen layer.

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\*\*\*Since the assumption of local thermodynamic equilibrium is employed, only those internal energies are considered which equilibrate readily with the translational energy.

(iii) The internal energy associated with the rotational and vibrational modes readily equilibrates with translational energy.

The interaction model at the gas-solid interface, with the various fluxes sketched in Figure 1, can be mathematically stated for dissociated air as provided through the following equations.

For a recombining atom:

$$F_A = F_A^\dagger + (1-\theta_A) F_A^\dagger + (\theta_A - \gamma_A) F_A^W ; A = O, N \quad (1)$$

For a molecule gaining from the corresponding atom recombination:

$$F_M = F_M^\dagger + (1-\theta_M) F_M^\dagger + \theta_M F_M^W + \gamma_A F_A^W ; M = O_2, N_2 \quad (2)$$

For all other atoms and molecules (surface is assumed to be noncatalytic with respect to them):

$$F_i = F_i^\dagger + (1-\theta_i) F_i^\dagger + \theta_i F_i^W \quad (3)$$

where  $F_i$  denotes a convective property such as mass, momentum, or energy.

Summing over all the species, we obtain from Eq. (1), (2), and (3), the following expression for the net flux of momentum or energy:

$$\sum_{i=1}^{NS} F_i = \sum_{i=1}^{NS} F_i^\dagger + \sum_{i=1}^{NS} (1-\theta_i) F_i^\dagger + \sum_{i=1}^{NS} \theta_i F_i^W. \quad (4)$$

That is, the net flux at the outer edge of the Knudsen layer equals the incident flux, plus the specularly reflected flux (incident minus the fraction that sticks) at the wall, plus the diffusely reflected flux (those that accommodate to the wall) from the wall.

Each species is treated separately in the mass balance equations. Therefore, Eqs. (1), (2), or (3) are employed depending on the species being considered. In Eq. (1), the diffusely reflected flux consists of those atoms that are accommodated to the wall minus those that recombine. For the molecules in Eq. (2), the diffusely reflected term is present along with the source term resulting from the appropriate atoms recombining on the surface.

#### VARIOUS FLUXES AND THE DISTRIBUTION FUNCTIONS

The interaction model of Eqs. (1) through (4) is employed to obtain the slip boundary equations at the gas/solid interface. Through Eq.(1), the net fluxes of species, momentum, and energy at the outer edge of the Knudsen layer are equated to the difference between the incident and reflected fluxes at the wall. These fluxes are assumed to be constant across the Knudsen layer and are obtained from moments of the distribution function. For a convected property  $\phi^i(\vec{v})$  such as mass, momentum, or energy for the  $i$ th species, the net flux of that property normal to the wall at the outer edge of the Knudsen layer, for example, is

$$F_i = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} v_y^i \phi^i(\vec{v}) f_s^i(\vec{v}) d^3v^i \quad (5)$$

where  $v_y^i$  is the normal component of the molecular velocity and  $f_s^i$  is the velocity distribution function at the edge of the Knudsen layer.

Similar integrals are obtained for the incident and reflected fluxes by

integrations over appropriate half-spaces in molecular velocity:

Incident flux:

$$F_i^\dagger = \int_{-\infty}^{\infty} \int_{-\infty}^0 \int_{-\infty}^{\infty} v_y^i \phi^i(\vec{V}) f_s^i(\vec{V}) d^3V^i \quad (6)$$

Specularly reflected flux:

$$F_i^\dagger = \int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} v_y^i \phi^i(\vec{V}) f_s^i(v_x, -v_y, v_z) d^3V^i \quad (7)$$

Diffusely reflected flux:

$$F_i^w = \int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} v_y^i \phi^i(\vec{V}) f_w^i(\vec{V}) d^3V^i \quad (8)$$

where  $f_w^i$  is the Maxwellian velocity distribution function.

The velocity distribution functions used in integrals contained in relations (5) through (8) are those for a nonuniform multicomponent mixture perturbed out of equilibrium:

$$f^i(\vec{V}) = f^{(0)i}(\vec{V}) [1 + \phi^i(\vec{V})] \quad (9)$$

where  $f^{(0)i}(\vec{V})$  is the Maxwellian distribution function for the  $i$ th species given as

$$f^{(0)i}(\vec{V}) = \frac{n_i m_i^{3/2}}{(2\pi kT)^{3/2}} e^{-(m_i/2kT)V_i^2} \quad (10)$$

and

$$\Phi^i(\vec{V}) = - A_k^i \frac{\partial(\ln T)}{\partial x_k} - B_{k\ell}^i \frac{\partial v_{0k}}{\partial x_\ell} + n \sum_{j=1}^{NS} C_k^{i(j)} d_k^j \quad (11)$$

Here  $k$  and  $\ell$  are the dummy indices for three coordinate directions and the summations with index  $j$  represents summation over all the species. The summation convention for repeated indices is used. The coefficients  $A_k^i$ ,  $B_{k\ell}^i$ , and  $C_k^{i(\ell)}$  are functions of the dimensionless velocity:

$$w_k^i = \sqrt{\frac{m_i}{2kT}} v_k^i \quad (12)$$

and are defined as

$$A_k^i = [a_{i0} + a_{i1}(\frac{5}{2} - w_i^2)] w_k^i \quad (13)$$

$$B_{k\ell}^i = b_{i0} (w_k^i w_\ell^i - \frac{1}{3} w_i^2 \delta_{k\ell}) \quad (14)$$

$$C_k^{i(j)} = c_{i0}^{(j)} w_k^i \quad (15)$$

where  $a_{i0}$ ,  $a_{i1}$ ,  $b_{i0}$ , and  $c_{i0}^{(j)}$  are constants determined from the variational problem in the first approximation for a mixture as given in ref. 7 and  $\delta_{k\ell}$  is the Kronecker delta such that

$$\begin{aligned} \delta_{k\ell} &= 1, \text{ if } k = \ell \\ \delta_{k\ell} &= 0, \text{ if } k \neq \ell. \end{aligned}$$

These constants are functions of the collision integrals and are related to the transport properties. The simplified form of these constants is provided in Appendix A of this paper. More details can be found in Appendix A of Ref. 2, or in Ref. 7. The diffusion vector  $d_k^j$  in Eq. (11) is related to the diffusion velocity of the  $j$ th species and is defined after neglecting the external forces as (Ref. 7):

$$d_k^j = \frac{\partial}{\partial x_k} \left( \frac{n_j}{\bar{n}} \right) + \left( \frac{n_j}{\bar{n}} - \frac{n_j m_j}{\rho} \right) \frac{\partial}{\partial x_k} (\ln p) \quad (16)$$

where  $n_j$  and  $m_j$  are, respectively, the number density and mass of the  $j$ th species,  $\bar{n}$  is the total number density  $\bar{n} = \sum_j n_j$ ,  $\rho$  is the total mass density  $\rho = \sum_j n_j m_j$ , and  $p$  is the total pressure  $p = \sum_j p_j$ . A simplified form for  $d_k^j$  is provided in Appendix A.

The total mass averaged velocity  $v_{0k}$  (i.e. the  $k$ th component) appearing in Eq. (11) is defined as

$$v_{0k} = \frac{1}{\rho} \sum_{j=1}^{NS} n_j m_j \bar{v}_k^j$$

where  $\bar{v}_k^j$  is the mean of total velocity  $v_k^j = v_{0k} + v_k^j$  of the  $j$ th species averaged over the distribution function and  $v_k^j$  is the thermal (or peculiar) velocity, also introduced in Eq. (5). The thermal velocity  $v_k^j$  of the  $j$ th species averaged over the distribution function is known as the diffusion velocity  $\bar{v}_k^j$ :



$$\bar{v}_k^j = \frac{1}{n_j} \int \int \int v_k^j \phi^j(\vec{v}) f^j(\vec{v}) d^3 v^j \quad (17)$$

A simplified expression for the diffusion velocity in terms of transport properties is provided in Appendix A.

### THE BALANCE AND SLIP EQUATIONS

Based on Eqs. (1) through (4), the balance equations for the  $i$ th species for fluxes normal to the surface of the species mass  $M_{iy}$ , the normal component of momentum  $P_{iy}$ , the tangential component of momentum  $P_{i||}$ , and the energy  $E_{iy}$  are obtained as follows:

#### (a) Species mass flux

For a recombining atom

$$M_{Ay} = \theta_A M_A^+ + (\theta_A - \gamma_A) M_A^W ; \quad A = O, N \quad (18)$$

For a molecule gaining from the corresponding atom recombination

$$M_{My} = \theta_M M_M^+ + \theta_M M_M^W + \gamma_A M_A^W ; \quad M = O_2, N_2 \quad (19)$$

For all other atoms and molecules

$$M_{iy} = \theta_i M_i^+ + \theta_i M_i^W \quad (20)$$

#### (b) Normal momentum flux

$$\sum_{i=1}^{NS} P_{iy} = \sum_{i=1}^{NS} (2-\theta_i) P_i^+ + \sum_{i=1}^{NS} \theta_i P_i^W = P_y \quad (21)$$

(c) Tangential momentum flux

$$\sum_{i=1}^{NS} P_{i||} = \sum_{i=1}^{NS} \theta_i P_{i||}^{\dagger} \quad (22)$$

(d) Energy flux<sup>†</sup>

$$\begin{aligned} E_y &= \sum_{i=1}^{NS} E_{iy} = \sum_{i=1}^{NS} E_{iy}^T + \sum_i e_{iy} M_{iy} \\ &= \sum_{i=1}^{NS} \theta_i E_i^T + \sum_{i=1}^{NS} \theta_i E_i^{Tw} + \sum_i \theta_i e_i^s M_i^{\dagger} \\ &\quad \text{diatomic molecules} \\ &\quad + \sum_i \theta_i e_i^w M_i^w \\ &\quad \text{diatomic molecules} \end{aligned} \quad (23)$$

where  $e_i$  is the internal energy of  $i$ th species that readily equilibrates with the translational energy  $E_i^T$  under the assumption of local thermodynamic equilibrium. For example,

$$e_i^{\text{rotation}} = \frac{kT}{m_i}$$

In writing the energy flux balance of Eq. (23) it has been assumed that there is no change in internal energy during specular reflection.

In obtaining Eqs. (18) through (23) we have used the following relations

---

<sup>†</sup>The energy balance is based on the assumption that the various energies considered readily equilibrate with the translational energy.

$$M_i^\dagger = -M_i^\dagger, \quad P_{i||}^\dagger = -P_{i||}^\dagger$$

$$E_i^\dagger = -E_i^\dagger, \quad P_{i||}^W = 0, \quad \text{and} \quad P_{iy}^\dagger = P_{iy}^\dagger$$

Because it is assumed that the atoms are consumed at the wall by catalytic recombination in Eq. (18), the net mass flux  $M_{Ay} \neq 0$ . Similarly, the net mass flux  $M_{My} \neq 0$  in Eq. (19). However,  $M_{iy} = 0$  in Eq. (20) for the atoms and molecules for whom the surface is assumed noncatalytic.

By substituting Eqs. (5), (6), (7) and (8) with the definition of  $\phi_i^\dagger(\vec{V})$  as mass for Eqs. (18) through (20), as normal component of momentum for Eq. (21), as tangential component of momentum for Eq. (22) and as energy for Eq. (23), respectively, and carrying out the integrations<sup>†</sup>, one obtains equations relating the slip properties to wall properties and gradients at the edge of Knudsen layer. All accommodation coefficients  $\theta_i$  are assumed to be equal to  $\theta$ .

Number density (or concentration) slip (obtained from mass flux balance):

$$\frac{n_i^s}{n_i^w} = \frac{2 \left[ 1 + \frac{1}{2} \frac{M_{iy}}{n_i^w m_i} \sqrt{\frac{2\pi m_i}{kT_w}} \right]}{\left( \frac{P_{iy}}{P_i^s} + 1 \right)} \sqrt{\frac{T_w}{T_s}} \quad (24)$$

Pressure slip (obtained from the flux balance of normal component of momentum)

<sup>†</sup>The mass, momentum, and energy fluxes in terms of evaluated integrals over the distribution function are given in Appendix B.

$$\begin{aligned}
p_s = & \left\{ -\frac{\theta}{3} \left[ \mu \left( \frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right) \right]_s \right. \\
& + \frac{2-\theta}{\sqrt{\pi}} \left[ k \frac{\partial T}{\partial y} \sum_{i=1}^{NS} n_i \left( a_{i0} - \frac{1}{2} a_{i1} \right) \right]_s + \frac{\theta}{2} p^w \\
& \left. / \left\{ \frac{\theta}{2} + \frac{2-\theta}{\sqrt{\pi}} \sum_i \left[ n_i \sum_{j=1}^{NS} c_{i0}^{(j)} d_y^j \right]_s \right\} \right\} \quad (25)
\end{aligned}$$

with viscosity  $\mu = \frac{1}{2} kT \sum_{i=1}^{NS} n_i b_{i0}$

Velocity slip (obtained from the flux balance of tangential component of momentum)

$$\begin{aligned}
v_{0x}^s = & \left\{ \sqrt{\pi} \left( \frac{2-\theta}{2\theta} \right) \mu_s \left( \frac{\partial v_{0x}}{\partial y} + \frac{\partial v_{0y}}{\partial x} \right)_s \right. \\
& + \frac{1}{2} \sum_{i=1}^{NS} p_i^s \left[ \frac{\partial \ln T}{\partial x} \left( a_{i0} - \frac{1}{2} a_{i1} \right) - \bar{n} \sum_{j=1}^{NS} c_{i0}^{(j)} d_x^j \right]_s \\
& \left. / \sum_{i=1}^{NS} \left( p_i^s \sqrt{\frac{m_i}{2kT_s}} \right) \right\} \quad (26)
\end{aligned}$$

$$\begin{aligned}
v_{0z}^s = & \left\{ \sqrt{\pi} \left( \frac{2-\theta}{2\theta} \right) \mu_s \left( \frac{\partial v_{0z}}{\partial y} + \frac{\partial v_{0y}}{\partial z} \right)_s \right. \\
& + \frac{1}{2} \sum_{i=1}^{NS} p_i^s \left[ \frac{\partial \ln T}{\partial z} \left( a_{i0} - \frac{1}{2} a_{i1} \right) - n \sum_{j=1}^{NS} c_{i0}^{(j)} d_z^j \right]_s \\
& \left. / \sum_{i=1}^{NS} \left( p_i^s \sqrt{\frac{m_i}{2kT_s}} \right) \right\}
\end{aligned}$$

$$/ \sum_{i=1}^{NS} (p_i^S \sqrt{\frac{m_i}{2kT_s}}) \quad (27)$$

Temperature slip:

$$(2kT_s)^{3/2} = \left[ -2\sqrt{\pi} \left( \frac{2-\theta}{2\theta} \right) \left( \sum_{i=1}^{NS} E_{iy} \right) + (2kT_w)^{3/2} \sum_{i=1}^{NS} \frac{n_i^w}{\sqrt{m_i}} \right] \\ / \left[ \sum_{i=1}^{NS} \frac{n_i^S}{\sqrt{m_i}} \left\{ 1 + \frac{1}{4} b_{i0} \left( \frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right) \right\} \right] \quad (28)$$

Equations (24) through (28) differ from the corresponding expressions provided in Ref. 2 due to small errors and also due to the differences in the interaction model employed at the gas-solid interface.

The constants  $a_{i0}$ ,  $a_{i1}$ ,  $b_{i0}$ , and  $c_{i0}^{(j)}$  (also known as the Sonine expansion coefficients) appearing in Eqs. (24) through (28) may now be expressed in terms of the transport properties as given in Appendix A. Using these relations along with the various flux expressions of Appendix B and also expressing  $d_k$  in terms of the gradient of mass fractions  $\partial C_j / \partial y$  as given in Appendix A (by neglecting diffusion due to pressure gradients and external forces), the following equations are obtained after some algebraic simplifications:<sup>§</sup>

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<sup>§</sup>The approximations made in the expressions for  $a_{i1}$  and  $b_{i0}$  are given in Appendix A.

Number density (or concentration) slip

Same as Eq. (24).

Pressure slip

$$\begin{aligned}
 p^s = & \left\{ -\frac{\theta}{3} \left[ \mu \left( \frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right) \right]_s + \frac{2}{5} \left( \frac{2-\theta}{\sqrt{\pi}} \right) \left[ \frac{1}{\bar{n}} \frac{\partial T}{\partial y} \sum_{i=1}^{NS} n_i K_i \sqrt{\frac{m_i}{2kT}} \right]_s \right. \\
 & \left. + \frac{\theta}{2} p^w \right\} / \left\{ \frac{\theta}{2} + 2 \left( \frac{2-\theta}{\sqrt{\pi}} \right) \sum_{i=1}^{NS} \sqrt{\frac{m_i}{2kT}} \right. \\
 & \left. \times \sum_{\substack{j=1 \\ j \neq i}}^{NS} D_{ij} \left[ \frac{\partial C_j}{\partial y} - C_j \sum_{q=1}^{NS} \left( \frac{\bar{m}}{m_q} \frac{\partial C_q}{\partial y} \right) \right]_s \right\} \quad (29)
 \end{aligned}$$

Velocity Slip

$$\begin{aligned}
 v_{0x}^s = & \left\{ \sqrt{\frac{\pi}{2}} \left( \frac{2-\theta}{\theta} \right) \left[ \frac{\mu}{\sqrt{kT}} \left( \frac{\partial v_{0x}}{\partial y} + \frac{\partial v_{0y}}{\partial x} \right) \right]_s + \frac{1}{5} \left[ \frac{1}{\bar{n}kT} \frac{\partial T}{\partial x} \right. \right. \\
 & \left. \times \sum_{i=1}^{NS} n_i \sqrt{m_i} K_i \right]_s - \bar{n}_s \sum_{i=1}^{NS} m_i \sum_{\substack{j=1 \\ j \neq i}}^{NS} D_{ij} \left[ \frac{\partial C_j}{\partial x} \right. \\
 & \left. \left. - C_j \sum_{q=1}^{NS} \left( \frac{\bar{m}}{m_q} \frac{\partial C_q}{\partial x} \right) \right]_s \right\} / \sum_{i=1}^{NS} n_i^s \sqrt{m_i} \quad (30) \\
 v_{0z}^s = & \left\{ \sqrt{\frac{\pi}{2}} \left( \frac{2-\theta}{\theta} \right) \left[ \frac{\mu}{\sqrt{kT}} \left( \frac{\partial v_{0z}}{\partial y} + \frac{\partial v_{0y}}{\partial z} \right) \right]_s + \frac{1}{5} \left[ \frac{1}{\bar{n}kT} \frac{\partial T}{\partial z} \right. \right.
 \end{aligned}$$

$$\begin{aligned}
& \times \sum_{j=1}^{NS} n_i \sqrt{m_i} K_i]_s - \bar{n}_s \sum_{i=1}^{NS} \sqrt{m_i} \sum_{\substack{j=1 \\ j \neq i}}^{NS} D_{ij} \left[ \frac{\partial C_j}{\partial z} \right. \\
& \left. - C_j \sum_{q=1}^{NS} \frac{\bar{m}}{m_q} \frac{\partial C_q}{\partial z} \right]_s \} / \sum_{i=1}^{NS} n_i^s \sqrt{m_i} \quad (31)
\end{aligned}$$

Temperature slip

$$\begin{aligned}
\frac{T_s}{T_w} = & \left\{ -\frac{\sqrt{\pi}}{\bar{n}_s} \sum_{i=1}^{NS} \frac{M_{iy}}{m_i} - \frac{\sqrt{\pi}}{2\bar{n}_s} \sum_{\substack{i \\ \text{diatomic} \\ \text{molecules}}} \left( \frac{m_i e_i^w}{kT_w} \right) \frac{M_{iy}}{m_i} - \frac{\sqrt{\pi}}{2\bar{n}_s} \left( \frac{2-\theta}{\theta} \right) \right. \\
& \times \sum_{\substack{i \\ \text{diatomic} \\ \text{molecules}}} \left( \frac{m_i e_i^s}{kT_w} \right) \frac{M_{iy}}{m_i} + \frac{1}{4} \sum_{\substack{i \\ \text{diatomic} \\ \text{molecules}}} \sqrt{\frac{2kT_s}{m_i}} \left( \frac{\bar{m}_s}{m_i} \right) C_i^s \left[ \frac{(e_i^w - e_i^s) m_i}{kT_w} \right] \\
& \times \left( \frac{P_{iy}}{p_i^s} + 1 \right) + \frac{1}{2} \sum_{i=1}^{NS} \sqrt{\frac{2kT_s}{m_i}} \left( \frac{\bar{m}_s}{m_i} \right) C_i^s \left( \frac{P_{iy}}{p_i^s} + 1 \right) \} \\
& / \left\{ -\sqrt{\pi} \left( \frac{2-\theta}{\theta} \right) \left( \frac{1}{2} \frac{K}{p} \frac{\partial T}{\partial y} - \frac{5}{4} \sum_{i=1}^{NS} \frac{M_{iy}}{\bar{n} m_i} \right)_s \right. \\
& \left. + \frac{1}{4} \sum_{i=1}^{NS} \sqrt{\frac{2kT_s}{m_i}} \left( \frac{\bar{m}_s}{m_i} \right) C_i^s \left( 3 \frac{P_{iy}}{p_i^s} + 1 \right) \right\} \quad (32)
\end{aligned}$$

where the mass fraction  $C_i$  and the mass of a mixture molecule  $\bar{m}$  are defined, respectively, as

$$C_i = n_i m_i / \rho$$

and

$$\bar{m} = \left( \sum_{j=1}^{NS} C_j / m_j \right)^{-1}$$

Equations (24), (29), (30), (31), and (32) differ from Eqs. (25) through (28) of Reference 3. For dissociated air, the gas-surface interaction model employed in Reference 3 appears to be inconsistent. Further, the diffusion vector  $d_k^j$  appears to have been incorrectly evaluated in Reference 3. If one carries out the simplifications in Eqs. (23), (24), and (28) of Reference 3 (which contain the binary assumption) through the evaluation of  $\frac{\partial}{\partial y} (n_j/n)$  in terms of mass fractions as given by Eqs. (35), (36), and (39) of the same reference, erroneous results are obviously obtained because

$\sum_{j=1}^{NS} (\partial C_j / \partial r)_s$  (which is zero by definition) is contained as a factor in several of these equations.

For the first-order recombination at the surface, the following relation between the atom mass flux  $M_{Ay}$  and the wall number density  $n_A^w$  may be employed

$$M_{Ay} = - k_{wA} (n_A^w m_A) \quad (33)$$

where the minus sign indicates that the flux is in the direction opposite to the outward normal and the expression for the rate constant  $k_{wA}$  with



diffusion and slip is (Ref. 2).<sup>††</sup>

$$k_{wA} = \gamma_A \sqrt{\frac{kT_w}{2\pi m_A}} \quad (34)$$

Here  $\gamma_A$  is the recombination coefficient.

For a fully catalytic wall ( $\gamma_A = 1$ ), the maximum value of the rate constant  $k_{wi}$  is limited by the surface temperature. The reaction rate constant for a fully catalytic wall with the gas phase in chemical equilibrium is often assumed to be infinity for the sake of simplicity.

Employing Eq. (33), the net mass flux  $M_{iy}$  appearing in Eqs. (24) and (32) may be defined as

$$M_{Ay} = -k_{wA} n_A^w m_A; \quad A = O, N \quad (35a)$$

$$M_{My} = k_{wA} n_A^w m_A; \quad \begin{cases} A = O \text{ for } M = O_2 \\ A = N \text{ for } M = N_2 \end{cases} \quad (35b)$$

For all other atoms and molecules,

$$M_{iy} = 0 \quad (35c)$$

Equation (24), with  $M_{iy}$  defined by Eqs. (35a) through (35c), gives

<sup>††</sup>As shown in ref. 2, by neglecting slip but keeping diffusion, a slightly different form of Eq. (34) is obtained:

$$k_{wA} = \left( \frac{2\gamma_A}{2-\gamma_A} \right) \sqrt{\frac{kT_w}{2\pi m_A}}$$

the number density ratio  $n_i^S/n_i^W$ . However, to obtain  $n_i^W$  from this ratio, an expression for  $n_i^S$  is required.

The net mass flux of O and N atoms to the surface,  $M_{Ay}$ , is also equal to the rate of consumption of these atoms at the wall from surface recombination:

$$M_{Ay} = \gamma_A M_{Ay}^+ ; \quad A = O, N \quad (36a)$$

and the corresponding net mass flux of  $O_2$  and  $N_2$  molecules will be

$$M_{My} = -\gamma_A M_{Ay}^+ ; \quad \begin{cases} A = O \text{ for } M = O_2 \\ A = N \text{ for } M = N_2 \end{cases} \quad (36b)$$

For all other species, the net mass flux to the surface may be assumed to be zero. Thus,

$$M_{iy} = 0 \quad (36c)$$

Substituting values of the net and incident fluxes  $M_{iy}$ ,  $M_{iy}^+$  from Appendix B in Eq. (36), the following expression is obtained (after we neglect thermal diffusion):

$$\sum_{\substack{j=1 \\ j \neq i}}^{NS} D_{ij}^S \left[ \frac{\partial C_j}{\partial y} - C_j \sum_{q=1}^{NS} \left( \frac{\bar{m}}{m_q} \frac{\partial C_q}{\partial y} \right) \right]_s = \frac{\psi_i^S}{m_i} \quad (37)$$

which may be used to obtain  $n_i^S$ .<sup>§</sup> Here  $\psi_i^S$  is the source term defined as:

$$\psi_A^S = -\frac{\gamma_A}{(2-\gamma_A)} \frac{1}{\sqrt{\pi}} \frac{m_A n_A^S}{2\bar{n}_S} \sqrt{\frac{2kT_S}{m_A}} \left( \frac{p_{Ay}}{p_A^S} + 1 \right) \quad (38a)$$

For  $O_2$  and  $N_2$  molecules

$$\psi_M^S = -\psi_A^S ; \quad \begin{cases} A = O & \text{for } M = O_2 \\ A = N & \text{for } M = N_2 \end{cases} \quad (38b)$$

For all other species

$$\psi_i^S = 0 \quad (38c)$$

#### SIMPLIFICATIONS FOR A MULTICOMPONENT MIXTURE

Equations (24) (29), (30), (31), and (32) for multicomponent gas flows can be simplified if one makes the following assumptions:

(i) All the diffusion coefficients,  $D_{ij}$ , for a multicomponent gas have

<sup>§</sup>If no assumption is made about  $D_{ij}$ , Eq. (37) would give an expression for  $(\partial C_i / \partial y)_S$  for all the species:

$$\left( \frac{\partial C_i}{\partial y} \right)_S = \left( \frac{m_i}{\bar{m}_S} \right) \left\{ \sum_{\substack{j=1 \\ j \neq i}}^{NS} D_{ij}^S \left[ \frac{\partial C_j}{\partial y} - C_j \sum_{\substack{q=1 \\ q \neq i}}^{NS} \frac{\bar{m}}{m_q} \frac{\partial C_q}{\partial y} \right]_S - \frac{\psi_i}{m_i} \right\} / \sum_{\substack{j=1 \\ j \neq i}}^{NS} (D_{ij} C_j)_S$$

The source term  $\psi_i$  in this expression, however, may be simplified to yield an expression for  $C_A^S$  (or  $n_A^S$ ) for the recombining atoms only:

$$C_A^S = \frac{m_A n_A^S}{\rho_S} = -2\sqrt{\pi} \left( \frac{2-\gamma_A}{\gamma_A} \right) \left( \frac{m_A}{\bar{m}_S} \right) \sqrt{\frac{m_A}{2kT_S}} \sum_{\substack{j=1 \\ j \neq A}}^{NS} D_{Aj}^S \left[ \frac{\partial C_j}{\partial y} - C_j \sum_{q=1}^{NS} \left( \frac{\bar{m}}{m_q} \frac{\partial C_q}{\partial y} \right) \right]_S$$

the same value so that  $D_{ij} = D_{12}$ ,<sup>†</sup>  $D_{12}$  is the same as the binary diffusion coefficient  $D_{12}$ .

- (ii) The normal momentum flux to the pressure ratio,  $P_{iy}/P_i$  is the same for all species and equal to that of the mixture. This also implies that the normal shear stress  $\tau_{yyi}$  for species  $i$  is the same as that for the mixture ( $\tau_{yy}$ ).
- (iii) The rotational and vibrational states are fully excited so that the internal energy  $e_i$  for the air molecule may be taken as equal to  $2kT/m_i$ .

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<sup>†</sup>This is a somewhat stronger assumption. Because  $D_{ij}$  are concentration dependent, whereas  $D_{ij}$  are virtually independent of composition. The multi-component diffusion coefficient  $D_{ij}$  is related to the binary diffusion coefficient  $D_{ij}$  through the following relations (see Ref. 7):

$$D_{ij} = \bar{K}_{ij} - (M_i/M_j) \bar{K}_{ji}$$

where quantities  $\bar{K}_{ij}$  are coefficients in a matrix which is the inverse of the matrix with the following coefficients:

$$\begin{aligned} K_{ij} &= \frac{C_i}{D_{ij}} + M_j \sum_{\substack{q=1 \\ q \neq i}}^{NS} \frac{C_q}{M_q D_{iq}} & (i \neq j) \\ &= 0 & (i=j) \end{aligned}$$

One can see, therefore, that by employing  $D_{12}$  (which is same as  $D_{12}$ ) for all the species in a multicomponent gas mixture, considerable saving is obtained in computational effort and time without losing the general flavor of multicomponent diffusion. This is particularly true if the dissociated air consists predominantly of nitrogen molecules and oxygen atoms. The shuttle entry conditions fall into this category. Simple and multicomponent diffusion gave same results in "An Experimental and Analytical Study of Slip and Catalytic Boundary Conditions Applied to Spheres in Low Reynolds Number Arc Jet Flows," by Carl D. Scott, Proceedings of the 9th International Symposium on Rarefied Gas Dynamics, Gottingen, July 15-20, 1974, pp. D.14-1 to 11.

These assumptions retain the major effects of multicomponent fluxes on various slip quantities and provide considerable saving in computational effort required for the analysis of a flow problem (ref. 2 and footnote on page 20). With these simplifications, Eqs. (24), (29), (30), (31) and (32) yield:

Concentration slip

$$\frac{n_i^s}{n_i^w} = 2 \left[ 1 + \frac{1}{2} \frac{M_i y}{n_i^w m_i} \sqrt{\frac{2\pi m_i}{kT_w}} \right] \sqrt{\frac{T_w}{T_s}} / \left( \frac{p_y}{p^s} + 1 \right) \quad (39)$$

Pressure slip

$$\begin{aligned} \frac{p^s}{p^w} = & \left\{ \frac{\theta}{2} - \frac{\theta}{3\bar{n}_w kT_w} \left[ \mu \left( \frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right) \right]_s + \frac{2}{5} \left( \frac{2-\theta}{\sqrt{\pi}} \right) \frac{1}{\bar{n}_w kT_w} \right. \\ & \times \left[ \frac{1}{\sqrt{2kT}} \frac{\partial T}{\partial y} \sum_{i=1}^{NS} \frac{n_i K_i}{\bar{n}} \sqrt{m_i} \right]_s \left. \right\} / \left\{ \frac{\theta}{2} - \frac{2(2-\theta)}{\sqrt{\pi}} \frac{D_{12}^s}{\sqrt{2kT_s}} \sum_{i=1}^{NS} \sqrt{m_i} \right. \\ & \times \left. \left[ \frac{\partial C_i}{\partial y} + (1-C_i) \sum_{q=1}^{NS} \left( \frac{\bar{m}}{\bar{m}_q} \frac{\partial C_q}{\partial y} \right) \right]_s \right\} \quad (40) \end{aligned}$$

Velocity slip

$$\begin{aligned} v_{0x}^s = & \left\{ \sqrt{\frac{\pi}{2}} \left( \frac{2-\theta}{\theta} \right) \left[ \frac{\mu}{\sqrt{kT}} \left( \frac{\partial v_{0x}}{\partial y} + \frac{\partial v_{0y}}{\partial x} \right) \right]_s + \frac{1}{5} \left[ \frac{1}{kT} \frac{\partial T}{\partial x} \sum_{i=1}^{NS} \frac{n_i K_i}{\bar{n}} \sqrt{m_i} \right]_s \right. \\ & + \bar{n}_s D_{12}^s \sum_{i=1}^{NS} \sqrt{m_i} \left[ \frac{\partial C_i}{\partial x} + (1-C_i) \sum_{q=1}^{NS} \left( \frac{\bar{m}}{\bar{m}_q} \frac{\partial C_q}{\partial x} \right) \right]_s \left. \right\} / \sum_{i=1}^{NS} n_i^s \sqrt{m_i} \quad (41) \end{aligned}$$

$$v_{0z}^s = \left\{ \sqrt{\frac{\pi}{2}} \left( \frac{2-\theta}{\theta} \right) \left[ \frac{\mu}{\sqrt{kT}} \left( \frac{\partial v_{0z}}{\partial y} + \frac{\partial v_{0y}}{\partial z} \right) \right]_s + \frac{1}{5} \left[ \frac{1}{kT} \frac{\partial T}{\partial z} \sum_{i=1}^{NS} \frac{n_i K_i}{\bar{n}} \sqrt{m_i} \right]_s \right. \\ \left. + \bar{n}_s D_{12}^s \sum_{i=1}^{NS} \sqrt{m_i} \left[ \frac{\partial C_i}{\partial z} + (1-C_i) \sum_{q=1}^{NS} \left( \frac{\bar{m}}{m_q} \frac{\partial C_q}{\partial z} \right) \right]_s \right\} / \sum_{i=1}^{NS} n_i^s \sqrt{m_i} \quad (42)$$

Temperature slip

$$\frac{T_s}{T_w} = \left\{ - \frac{\sqrt{\pi}}{\bar{n}_s} \sum_{i=1}^{NS} \frac{M_{iy}}{m_i} - \frac{\sqrt{\pi}}{\bar{n}_s} \sum_i \frac{M_{iy}}{m_i} + \frac{1}{2} \left( \frac{p_y}{p^s} + 1 \right) \right. \\ \times \sum_i \sqrt{\frac{2kT_s}{m_i}} \left( \frac{\bar{m}_s}{m_i} \right) C_i^s + \frac{1}{2} \left( \frac{p_y}{p^s} + 1 \right) \sum_{i=1}^{NS} \sqrt{\frac{2kT_s}{m_i}} \left( \frac{\bar{m}_s}{m_i} \right) C_i^s \Big\} \\ \text{diatomic molecules} \\ / \left[ - \sqrt{\pi} \left( \frac{2-\theta}{\theta} \right) \left\{ \frac{1}{2} \frac{K}{p} \frac{\partial T}{\partial y} - \frac{5}{4} \sum_{i=1}^{NS} \left( \frac{M_{iy}}{\bar{n} m_i} \right) - \frac{1}{\bar{n}} \sum_i \frac{M_{iy}}{m_i} \right\}_s \right. \\ \text{diatomic molecules} \\ \left. + \frac{1}{4} \left( 3 \frac{p_y}{p^s} + 1 \right) \sum_{i=1}^{NS} \sqrt{\frac{2kT_s}{m_i}} \left( \frac{\bar{m}_s}{m_i} \right) C_i^s + \frac{1}{2} \left( \frac{p_y}{p^s} + 1 \right) \sum_i \sqrt{\frac{2kT_s}{m_i}} \left( \frac{\bar{m}_s}{m_i} \right) C_i^s \right] \\ \text{diatomic molecules} \quad (43a)$$

or, if the internal energy is frozen during reflection from the surface (see Eq. (28) of Ref. 5, for example),

$$\frac{T_s}{T_w} = \left\{ - \frac{\sqrt{\pi}}{\bar{n}_s} \sum_{i=1}^{NS} \frac{M_{iy}}{m_i} + \frac{1}{2} \left( \frac{p_y}{p^s} + 1 \right) \sum_{i=1}^{NS} \sqrt{\frac{2kT_s}{m_i}} \left( \frac{\bar{m}_s}{m_i} \right) C_i^s \right\} \\ / \left[ - \sqrt{\pi} \left( \frac{2-\theta}{\theta} \right) \left\{ \frac{1}{2} \frac{K}{p} \frac{\partial T}{\partial y} - \frac{5}{4} \sum_{i=1}^{NS} \left( \frac{M_{iy}}{\bar{n} m_i} \right) \right\}_s \right. \\ \left. + \frac{1}{4} \left( 3 \frac{p_y}{p^s} + 1 \right) \sum_{i=1}^{NS} \sqrt{\frac{2kT_s}{m_i}} \left( \frac{m_s}{m_i} \right) C_i^s \right] \quad (43b)$$

Equation (37) may also be simplified to yield an explicit expression for  $n_i^S$ :

$$n_i^S = \frac{\rho_S}{m_i} \left[ 1 + \frac{\left(\frac{\partial C_i}{\partial y}\right)_S + \frac{1}{m_i} \left(\frac{\psi_i}{D_{12}}\right)_S}{\sum_{q=1}^{NS} \left(\frac{\bar{m}}{m_q} \frac{\partial C_q}{\partial y}\right)_S} \right] \quad (44)$$

where

$$\psi_A^S = -\frac{\gamma_A}{(2-\gamma_A)} \frac{1}{\sqrt{\pi}} \frac{m_A n_A^S}{2\bar{n}_S} \sqrt{\frac{2kT_S}{m_A}} \left( \frac{p_{Ay}}{p_A^S} + 1 \right) ; \quad A = O, N \quad (45a)$$

$$\psi_M^S = -\psi_A^S ; \quad \begin{cases} A = O \text{ for } M = O_2 \\ A = N \text{ for } M = N_2 \end{cases} \quad (45b)$$

$$\psi_i^S = 0 \text{ for all other species} \quad (45c)$$

It is suggested here that the concentration for the major specie (for example, nitrogen) be obtained by requiring the sum of concentrations of all the species to equal unity. It may be mentioned here that the mass of the  $i$ th species,  $m_i$ , is related to the molecular (or atomic) weight,  $W_i$ , through the relation

$$\frac{m_i}{W_i} = \frac{k}{R} \quad (46)$$

where  $k$  is the Boltzmann constant and  $R$  is the universal gas constant.

#### CONCENTRATION SLIP BOUNDARY CONDITION FOR A FULLY CATALYTIC AND A NONCATALYTIC SURFACE

Equation (44) gives slip values of the concentration  $n_i^S$  for a finite catalytic surface. For a fully catalytic ( $\gamma_A = 1$ ) surface one generally

assumes complete recombination of atoms at the surface. There is a slight discrepancy in this assumption because the maximum recombination rate is limited by the surface temperature as discussed earlier [See the discussion following Eq. (34)]. Thus, for a fully catalytic surface, equation (44) or (41) should be employed with  $\gamma_A = 1$ .

For a noncatalytic surface ( $\gamma_A = 0$ ), Eq. (45) gives  $\psi_i^S = 0$  for all the species. For this case, Eq. (44) becomes

$$n_i^S = \frac{\rho_s}{m_i} \left[ 1 + \frac{\left( \frac{\partial C_i}{\partial y} \right)_s}{\sum_{q=1}^{NS} \left( \frac{\bar{m}}{m_q} \frac{\partial C_q}{\partial y} \right)_s} \right] \quad (47a)$$

which may also be written as

$$\left( \frac{\partial C_i}{\partial y} \right)_s = - (1 - C_i^S) \sum_{q=1}^{NS} \left( \frac{\bar{m}}{m_q} \frac{\partial C_q}{\partial y} \right)_s \quad (47b)$$

Summing the above equation over all the species gives

$$\sum_{q=1}^{NS} \left( \frac{\bar{m}}{m_q} \frac{\partial C_q}{\partial y} \right)_s = 0 \quad (48)$$

for a noncatalytic surface. Therefore, Eq. (47a) is not an appropriate boundary condition. However, employing Eq. (48) with Eq. (47b) yields:

$$\left( \frac{\partial C_i}{\partial y} \right)_s = 0 \quad (49)$$



which may be used as the boundary condition for a noncatalytic surface with a multicomponent gas mixture.

### SIMPLIFICATIONS FOR A BINARY MIXTURE

At lower altitudes with the flow in slight nonequilibrium (i.e. when the Reynolds number parameter  $\epsilon^2 \ll 1$ ), the derivatives of various quantities with respect to  $x$  and  $z$  and some other higher order terms like  $\partial v_{0y}/\partial y$  may be dropped through an order of magnitude analysis (see Ref. 9, for example). Further, the dissociated air may be considered as a binary mixture (i.e. consisting of atoms and molecules only, see Ref. 8) at these altitudes. If an assumption is also made that the internal energy of the molecules remains frozen during reflection from the surface, Eqs. (39) through (45) can be simplified further to the forms given here.

Concentration slip

$$\frac{n_A^s}{n_A^w} = \left( \frac{2-\gamma_A}{2} \right) \sqrt{\frac{T_w}{T_s}} \quad (50)$$

Pressure Slip

$$\begin{aligned} \frac{p^s}{p^w} = & \left\{ 1 + \frac{4}{5\sqrt{\pi}} \left( \frac{2-\theta}{\theta} \right) \frac{1}{n_w k T_w} \left( \frac{\bar{m}}{\sqrt{2kT}} \frac{\partial T}{\partial y} \right)_s \right. \\ & \left. \left[ \frac{C_A^s K_A}{\sqrt{m_A}} + \frac{(1-C_A^s)}{\sqrt{m_M}} K_M \right] \right\} / \left\{ 1 - \frac{4}{\sqrt{\pi}} \left( \frac{2-\theta}{\theta} \right) \frac{D_{AM}^s}{\sqrt{2kT_s}} \right. \\ & \left. \times \frac{\bar{m}_s}{\sqrt{m_A m_M}} \left( \frac{\sqrt{m_M} - \sqrt{m_A}}{\sqrt{m_A m_M}} \right) \left( \frac{\partial C_A}{\partial y} \right)_s \right\} \quad (51) \end{aligned}$$

# Velocity Slip

$$v_{0x}^s = \left\{ \sqrt{\frac{\pi}{2}} \left( \frac{2-\theta}{\theta} \right) \left[ \frac{\mu}{\sqrt{\kappa T}} \frac{\partial v_{0x}}{\partial y} \right]_s \right\} / \{ (\sqrt{m_A} - \sqrt{m_M}) n_A^s + \bar{n}_s \sqrt{m_M} \} \quad (52a)$$

$$v_{0z}^s = \left\{ \sqrt{\frac{\pi}{2}} \left( \frac{2-\theta}{\theta} \right) \left[ \frac{\mu}{\sqrt{\kappa T}} \frac{\partial v_{0z}}{\partial y} \right]_s \right\} / \{ (\sqrt{m_A} - \sqrt{m_M}) n_A^s + \bar{n}_s \sqrt{m_M} \} \quad (53a)$$

# Temperature Slip

$$\begin{aligned} \frac{T_s}{T_w} = & \left\{ \sqrt{\frac{2kT_s}{m_A}} \left( \frac{\bar{m}_s}{m_A} \right) \left[ \left\{ 1 - 2 \left( \frac{m_A}{m_M} \right)^{3/2} \right\} C_A^s + 2 \left( \frac{m_A}{m_M} \right)^{3/2} \right] \right. \\ & + \sqrt{\frac{2kT_w}{m_A}} \left( \frac{\gamma_A n_A^w}{2\bar{n}_s} \right) \left( 1 - 2 \frac{m_A}{m_M} \right) \left. \right\} \\ & / \left\{ -\sqrt{\pi} \left( \frac{2-\theta}{\theta} \right) \left[ \frac{1}{2} \left( \frac{\kappa}{p} \frac{\partial T}{\partial y} \right)_s \right. \right. \\ & + \frac{1}{4\sqrt{\pi}} \left( 5 - 9 \frac{m_A}{m_M} \right) \sqrt{\frac{2kT_w}{m_A}} \left( \frac{\gamma_A n_A^w}{2\bar{n}_s} \right) \left. \right] + \sqrt{\frac{2kT_s}{m_A}} \left( \frac{\bar{m}_s}{m_A} \right) \\ & \times \left[ \left\{ 1 - 2 \left( \frac{m_A}{m_M} \right)^{3/2} \right\} C_A^s + 2 \left( \frac{m_A}{m_M} \right)^{3/2} \right] \left. \right\} \quad (54a) \end{aligned}$$

or, with frozen internal energy during surface reflection,

$$\begin{aligned}
 \frac{T_S}{T_W} = & \left\{ \sqrt{\frac{2kT_S}{m_A}} \left( \frac{\bar{m}_S}{m_A} \right) \left[ \left\{ 1 - \left( \frac{m_A}{m_M} \right)^{3/2} \right\} C_A^S \right. \right. \\
 & \left. \left. + \left( \frac{m_A}{m_M} \right)^{3/2} \right] + \sqrt{\frac{2kT_W}{m_A}} \left( \frac{\gamma_A n_A^W}{2\bar{n}_S} \right) \left( 1 - \frac{m_A}{m_M} \right) \right\} \\
 & / \left\{ -\sqrt{\pi} \left( \frac{2-\theta}{\theta} \right) \left[ \frac{1}{2} \left( \frac{K}{P} \frac{\partial T}{\partial y} \right)_S \right. \right. \\
 & \left. \left. + \frac{5}{4\sqrt{\pi}} \left( 1 - \frac{m_A}{m_M} \right) \sqrt{\frac{2kT_W}{m_A}} \left( \frac{\gamma_A n_A^W}{2\bar{n}_S} \right) + \sqrt{\frac{2kT_S}{m_A}} \left( \frac{\bar{m}_S}{m_A} \right) \right] \right. \\
 & \left. \times \left[ \left\{ 1 - \left( \frac{m_A}{m_M} \right)^{3/2} \right\} C_A^S + \left( \frac{m_A}{m_M} \right)^{3/2} \right] \right\} \quad (54b)
 \end{aligned}$$

In Eqs. (54a) and (54b),  $n_A^W$  is obtained from  $n_A^S$  by using Eq. (50).

Expression for  $n_A^S$

$$\begin{aligned}
 n_A^S = & \frac{\rho_S}{m_A} \left[ \left( \frac{1}{\bar{m}} + \frac{1}{m_A} - \frac{1}{m_M} \right) \frac{\partial C_A}{\partial y} \right. \\
 & \left. - \gamma_A \left( \sqrt{\frac{kT}{2\pi m_A}} \left( \frac{n_A}{\rho_{DAM}} \right) + \frac{1}{2m_A} \frac{\partial C_A}{\partial y} \right) \right]_S \\
 & / \left[ \left( \frac{1}{m_A} - \frac{1}{m_M} \right) \left( \frac{\partial C_A}{\partial y} \right)_S \right] \quad (55a)
 \end{aligned}$$

which may also be written as

$$\frac{n_A^s m_A}{\rho_s} = C_A^s = \left( \frac{2-\gamma_A}{2\gamma_A} \right) \sqrt{\frac{2\pi m_A}{kT_s}} D_{AM}^s \left( \frac{\partial C_A}{\partial y} \right)_s \quad (55b)$$

For a fully catalytic surface ( $\gamma_A = 1$ ), Eq. (55b) gives appropriate value for the concentration slip.<sup>†</sup> The relevant boundary condition for a noncatalytic surface ( $\gamma_A = 0$ ) will be

$$\left( \frac{\partial C_A}{\partial y} \right)_s = 0 \quad (56a)$$

as can readily be seen from Eq. (55b).

For a noncatalytic surface ( $\gamma_A = 0$ ), pressure and temperature slip Eqs. (51) and (54b) are further simplified, with the help of Eq. (56a), to:

Pressure slip

$$p^s = p^w + \frac{4}{5\sqrt{\pi}} \left( \frac{2-\theta}{\theta} \right) \left( \frac{\bar{m}}{\sqrt{2kT}} \frac{\partial T}{\partial y} \right)_s \left[ \frac{C_A^s K_A}{\sqrt{m_A}} + \frac{(1-C_A^s)}{\sqrt{m_M}} K_M \right] \quad (57a)$$

Temperature slip (with frozen internal energy during reflection from the surface)

$$T_s = T_w + \sqrt{\pi} \left( \frac{2-\theta}{2\theta} \right) \left\{ \frac{K}{k} \frac{1}{\sqrt{2kT}} \frac{\partial T}{\partial y} \right\}_s / \left[ \bar{m}_s \bar{n}_s \left\{ \left( \frac{1}{m_A^{3/2}} - \frac{1}{m_M^{3/2}} \right) C_A^s + \frac{1}{m_M^{3/2}} \right\} \right] \quad (58a)$$

<sup>†</sup>Sometimes in the literature  $C_A$  is prescribed as zero for a fully catalytic surface. Strictly speaking, this will be true only when the Reynolds number parameter  $\epsilon^2$  (Ref. 8) is approximately zero (close to the chemical equilibrium condition at low altitudes). This can easily be seen by nondimensionalising equation (55b) in a way similar to equation (28d) of reference 8. Thus, the recombination rate coefficient  $\gamma_A$  and density (as measured through  $\epsilon^2$ ), both control the recombination rate and not  $\gamma_A$  alone.

Equations (52a), (53a), (57a), and (58a) (with the noncatalytic surface assumption in Eqs. (57a) and (58a)) can be rewritten as:

Velocity slip

$$v_{0x}^s = A_1 a_1 \frac{1}{\bar{n}_s \sqrt{\bar{m}_s}} \left[ \frac{\mu}{\sqrt{kT}} \frac{\partial v_{0x}}{\partial y} \right]_s \quad (52b)$$

$$v_{0z}^s = A_1 a_1 \frac{1}{\bar{n}_s \sqrt{\bar{m}_s}} \left[ \frac{\mu}{\sqrt{kT}} \frac{\partial v_{0z}}{\partial y} \right]_s \quad (53b)$$

Pressure slip

$$p^s = p^w + B_1 b_1 \left( \frac{\bar{\gamma}-1}{\bar{\gamma}} \right) \left[ \frac{\sqrt{\bar{m}}}{\sqrt{kT}} K \frac{\partial T}{\partial y} \right]_s \quad (57b)$$

Temperature slip

$$T_s = T_w + C_1 c_1 \left( \frac{\bar{\gamma}-1}{\bar{\gamma}} \right) \left[ \frac{K}{k} \frac{1}{\sqrt{kT}} \frac{\partial T}{\partial y} / \frac{\bar{n}}{\sqrt{\bar{m}}} \right]_s \quad (58b)$$

where

$$A_1 = \frac{\bar{n}_s \sqrt{\bar{m}_s}}{(\sqrt{m_A} - \sqrt{m_M}) n_A^s + \sqrt{m_M} \bar{n}_s} \left( \frac{16}{5\pi} \right)$$

$$B_1 = \frac{\left[ \sqrt{\frac{m_A}{\bar{m}}} \frac{C_A K_A}{m_A} + \sqrt{\frac{m_M}{\bar{m}}} \frac{C_M K_M}{m_M} \right]_s}{\left[ \frac{C_A K_A}{m_A} + \frac{C_M K_M}{m_M} \right]_s} \left( \frac{64}{75\pi} \right) \left( \frac{\bar{\gamma}}{\bar{\gamma}-1} \right)$$

$$C_1 = \left[ \bar{m}^{3/2} \left\{ \left( \frac{1}{m_A^{3/2}} - \frac{1}{m_M^{3/2}} \right) C_A + \frac{1}{m_M^{3/2}} \right\} \right]^{-1} \left( \frac{128}{150\pi} \right) \left( \frac{\bar{\gamma}}{\bar{\gamma}-1} \right)$$

$$a_1 = \frac{5\pi}{16} \sqrt{\frac{\pi}{2}} \left(\frac{2-\theta}{\theta}\right) = 1.2304 \left(\frac{2-\theta}{\theta}\right)$$

$$b_1 = \frac{15}{16} \sqrt{\frac{\pi}{2}} \left(\frac{2-\theta}{\theta}\right) = 1.1750 \left(\frac{2-\theta}{\theta}\right)$$

$$c_1 = \frac{75\pi}{128} \sqrt{\frac{\pi}{2}} \left(\frac{2-\theta}{\theta}\right) = 2.3071 \left(\frac{2-\theta}{\theta}\right)$$

The concentration slip condition consistent with Eqs. (52b), (53b), (57b), and (58b) is

$$\left(\frac{\partial C_A}{\partial y}\right)_s = 0 \quad (56b)$$

The range of values of  $A_1$ ,  $B_1$ , and  $C_1$  is as given below for a mixture of oxygen atoms and molecules and  $\bar{\gamma} = 1.4$  (ref. 8):

$$1.0039 < A_1 < 1.0186$$

$$0.9507 < B_1 < (0.9507) \times \left( \sqrt{\frac{3}{4}} \frac{K_A}{m_A} + \sqrt{\frac{3}{2}} \frac{K_M}{m_M} \right) / \left( \frac{K_A}{m_A} + \frac{K_M}{m_M} \right)$$

$$0.9056 < C_1 < 0.9507$$

The minimum values for  $A_1$  and  $C_1$  occur at  $n_A = 0.5 \rho/m_A$ , whereas the maximum value for  $B_1$  occurs at this value of  $n_A$ .

The expression (52b), (57b), and (58b) reduce to those obtained in Ref. 8<sup>††</sup> if one assumes the values for  $A_1$ ,  $B_1$ , and  $C_1$  to be unity and a non

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<sup>††</sup> See Appendix C for the dimensional form of the slip boundary conditions given in Ref. 8.

catalytic surface boundary condition as given by Eq. (56b). The concentration slip boundary condition provided in Ref. 8 is:

$$C_A^S = C_{Ae}^S + \left( \frac{2-\gamma_A}{2\gamma_A} \right) \sqrt{\frac{2\pi m_A}{kT_s}} D_{AM} \frac{\partial C_A}{\partial n^*} \quad (59)$$

which is the same as Eq. (55b) obtained here except for the additive term  $C_{Ae}^S$ .<sup>†††</sup> It is obvious that the temperature slip boundary condition of Eq. (2.8b) obtained in Ref. 8 is valid, strictly speaking, for a noncatalytic surface only and is not consistent with the concentration slip boundary condition of Eq. (2.8c) (reproduced here as Eq. (59)) obtained for a finite catalytic wall. As a matter of fact, the velocity and temperature slip boundary conditions of Ref. 8 are similar to those of Ref. 9,<sup>§</sup> where these slip conditions are provided for a perfect gas (or single species mixture).

The inconsistencies in the boundary conditions used in Refs. 10 and 11 are similar to those of Ref. 8, namely, the pressure and temperature slip

<sup>†††</sup> It appears that Eq. (2.8d) of Ref. 8 for the concentration slip has been formulated for small deviations from the chemical equilibrium condition (i.e. the Reynolds number parameter  $\epsilon^2 \ll 1$ ). Thus, when flow goes to chemical equilibrium (with  $\epsilon^2 \approx 0$ ), one obtains from Eq. (2.8d) the equilibrium value for the concentration i.e.  $C_A = C_{Ae}$ , which would be zero for the oxygen atoms for surface temperatures of 2000°K or less.

<sup>§</sup> There appears to be some error with the form of Eqs. (2.7c) and (2.7d) given in Ref. 9 if one employs the definition of dimensionless heat-transfer rate 'q' in these equations from Eq. (2.4b) of the same reference. (The Reynolds number parameter,  $\epsilon^2$ , is missing in Eqs. (2.2b) and (2.4b) for dimensionless shear stress and heat-transfer, respectively, of the same reference. These have been corrected in Ref. 8.) The resulting pressure and temperature slip expressions will contain the dimensionless viscosity coefficient ' $\mu$ ' without the Prandtl number, see Ref. 10 and 11, for example. This is in contradiction to Eq. (2.8c) of Ref. 8, which contains dimensionless 'K' in place of dimensionless ' $\mu$ '. For a perfect gas, employing ' $\mu$ ' in place of 'K' in the pressure and temperature slip equations will result in no error. However, for real gas flows, the pressure and temperature slip values will be in error by the factor of  $\mu/K$ . The present analysis indicates that Eq. (2.8c) of Ref. 8 is of the "correct" form for a single species mixture.

values are in error by a factor of dimensionless viscosity to the thermal conductivity ratio ' $\mu/K$ '. References 10 and 11 also employ the single species formulation for obtaining the velocity, temperature and pressure slip values and the concentration slip expression in these references is that obtained for a binary mixture (Ref. 8). The coefficients appearing in the slip equations of Ref. 11 may be obtained by multiplying  $a_1$ ,  $b_1$ , and  $c_1$  (coefficients of Ref. 8) given here by  $16/5\pi$ . The factor  $16/5$  is sometimes replaced by  $\pi$ .

#### SIMPLIFICATIONS FOR A SINGLE SPECIES MIXTURE

Eqs. (39) through (42) and Eq. (43b) may be simplified for a single species mixture to the expressions obtained in Ref. 6. For small jump (or slip) conditions these simplified equations may be written as (with  $\gamma_A = 0$  and  $M_{iy} = 0$  for a single species mixture):

Density slip

$$\frac{\rho_s}{\rho_w} = \frac{\bar{m} \bar{n}^s}{\bar{m} \bar{n}^w} = \sqrt{\frac{T_w}{T_s}} \left\{ 1 + \left[ \frac{5}{24} \sqrt{\frac{\pi}{2}} \frac{\lambda_s}{\sqrt{RT_s}} \left( \frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right)_s \right] \right\}^{-1} \quad (60a)$$

Pressure slip

$$\frac{p^s}{p^w} = \left\{ 1 - \left[ \left( \frac{2-\theta}{\theta} \right) \frac{15}{16} \left( \frac{\lambda}{T} \frac{\partial T}{\partial y} \right)_s + \frac{5}{12} \sqrt{\frac{\pi}{2}} \frac{\lambda_s}{\sqrt{RT_s}} \right. \right. \\ \left. \left. \times \left( \frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right)_s \right] \right\}^{-1} \quad (61a)$$



Velocity slip

$$v_{0x}^s = \left(\frac{2-\theta}{\theta}\right) \left(\frac{5\pi}{16}\right) \lambda_s \left(\frac{\partial v_{0x}}{\partial y} + \frac{\partial v_{0y}}{\partial x}\right)_s + \frac{15}{32} \sqrt{\frac{\pi}{2} RT_s} \left(\frac{\lambda}{T} \frac{\partial T}{\partial x}\right)_s \quad (62)$$

$$v_{0z}^s = \left(\frac{2-\theta}{\theta}\right) \left(\frac{5\pi}{16}\right) \lambda_s \left(\frac{\partial v_{0z}}{\partial y} + \frac{\partial v_{0y}}{\partial z}\right)_s + \frac{15}{32} \sqrt{\frac{\pi}{2} RT_s} \left(\frac{\lambda}{T} \frac{\partial T}{\partial z}\right)_s \quad (63)$$

Temperature slip<sup>†</sup>

$$\frac{T_s}{T_w} = \frac{1}{2} \left(\frac{p_y}{p_s} + 1\right) \left\{ \left[-\frac{1}{2} + \frac{3}{4} \left(\frac{p_y}{p_s} + 1\right)\right] - \left[\frac{75\pi}{128} \left(\frac{2-\theta}{\theta}\right) \left(\frac{\lambda}{T} \frac{\partial T}{\partial y}\right)_s\right] \right\}^{-1} \quad (64a)$$

where we have used the following relations between the coefficients of viscosity and thermal conductivity and the mean free path for perfectly elastic spherical molecules (ref. 12).

$$\mu = \frac{5}{16} \sqrt{2\pi RT} \rho \lambda \quad (65a)$$

$$K = \frac{15}{4} \frac{k}{\bar{m}} \mu \quad (65b)$$

The expression for  $\mu$  given earlier, following Eq. (25), for a single species mixture is modified to:

$$\mu = \frac{1}{2} \bar{n} k T b_0$$

If, now, an assumption is made that the slip values are small, equations for the density, pressure, and temperature slip are simplified to:

<sup>†</sup>Since the temperature slip expression contained in Ref. 6 is for a gas consisting of perfectly elastic spherical molecules, the gas does not possess any internal degree of freedom. Therefore, we have obtained the temperature slip equation from Eq. (43b).

Density slip

$$\frac{\rho_s}{\rho_w} = \sqrt{\frac{T_w}{T_s}} \left\{ 1 - \frac{5}{24} \sqrt{\frac{\pi}{2}} \frac{\lambda_s}{\sqrt{RT_s}} \left( \frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right)_s \right\} \quad (60b)$$

Pressure slip

$$\frac{p^s}{p^w} = 1 + \left( \frac{2-\theta}{\theta} \right) \left( \frac{15}{16} \right) \left( \frac{\lambda}{T} \frac{\partial T}{\partial y} \right)_s - \frac{5}{12} \sqrt{\frac{\pi}{2}} \frac{\lambda_s}{\sqrt{RT_s}} \left( \frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right)_s \quad (61b)$$

Temperature slip

$$\frac{T_s}{T_w} = -\frac{1}{4} \left( \frac{p_y}{p^s} + 1 \right) + \frac{3}{8} \left( \frac{p_y}{p^s} + 1 \right)^2 + \frac{1}{2} \left( \frac{p_y}{p^s} + 1 \right) \left( \frac{75\pi}{128} \right) \left( \frac{2-\theta}{\theta} \right) \left( \frac{\lambda}{T} \frac{\partial T}{\partial y} \right)_s \quad (64b)$$

or,

$$\begin{aligned} \frac{T_s}{T_w} = & 1 + \left( \frac{2-\theta}{\theta} \right) \left( \frac{75\pi}{128} \right) \left( \frac{\lambda}{T} \frac{\partial T}{\partial y} \right)_s - \frac{5}{48} \sqrt{\frac{\pi}{2}} \frac{\lambda_s}{RT_s} \\ & \times \left( \frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right)_s \end{aligned} \quad (64c)$$

In obtaining Eq. (64c) from (64b), we have used  $p_y/p^s \approx 1$  in the second-order terms (i.e. 2nd and 3rd terms on right side of Eq. (64b)). Equations (61b), (62), (63), and (64c) are the slip equations given in refs. 6 and 12.

#### NO-SLIP BOUNDARY CONDITION FOR THE SPECIES CONCENTRATION

Multicomponent Mixture. The no-slip boundary condition for the species concentration without any assumptions may be obtained from Eqs. (44) and

(45). In the absence of slip, the Knudsen layer thickness shrinks to zero and the values at the top of the Knudsen layer become the wall values (see Fig. 1):

$$n_i^w = \frac{\rho_w}{m_i} \left[ 1 + \frac{\left(\frac{\partial C_i}{\partial y}\right)_w + \frac{1}{m_i} \left(\frac{\psi_i}{D_{12}}\right)_w}{\sum_{q=1}^{NS} \left(\frac{\bar{m}}{\bar{m}_q} \frac{\partial C_q}{\partial y}\right)_w} \right] \quad (66)$$

with

$$\psi_A^w = - \frac{2\gamma_A}{(2-\gamma_A)} \frac{1}{\pi} \frac{m_A n_A^w}{2 \bar{n}_w} \sqrt{\frac{2kT_w}{m_A}} \quad ; \quad A = O, N \quad (67a)$$

$$\psi_M^w = - \psi_A^w \quad ; \quad \begin{cases} A = O \text{ for } M = O_2 \\ A = N \text{ for } M = N_2 \end{cases} \quad (67b)$$

$$\psi_i^w = 0 \text{ for all other species} \quad (67c)$$

where we have neglected the higher order shear (i.e.  $P_y/p^w \approx 1$ ).

It is suggested here, again, that the concentration for the major specie (for example, nitrogen) be obtained by requiring the sum of concentrations of all the species to equal unity.

For the recombining O and N atoms, Eq. (66) may further be simplified to:

$$n_A^w = \frac{1}{k_{wA}} \left[ \bar{n} D_{12} \left\{ \frac{\partial C_A}{\partial y} + (1-C_A) \sum_{q=1}^{NS} \left( \frac{\bar{m}}{\bar{m}_q} \frac{\partial C_q}{\partial y} \right) \right\} \right]_w \quad (68)$$

The recombination rate constant  $k_{wA}$  in Eq. (68) has been defined as (Ref. 2)

$F_i^\downarrow$  = incident flux  
 $F_i^\uparrow$  = specularly reflected flux  
 $F_i^w$  = diffusely reflected flux

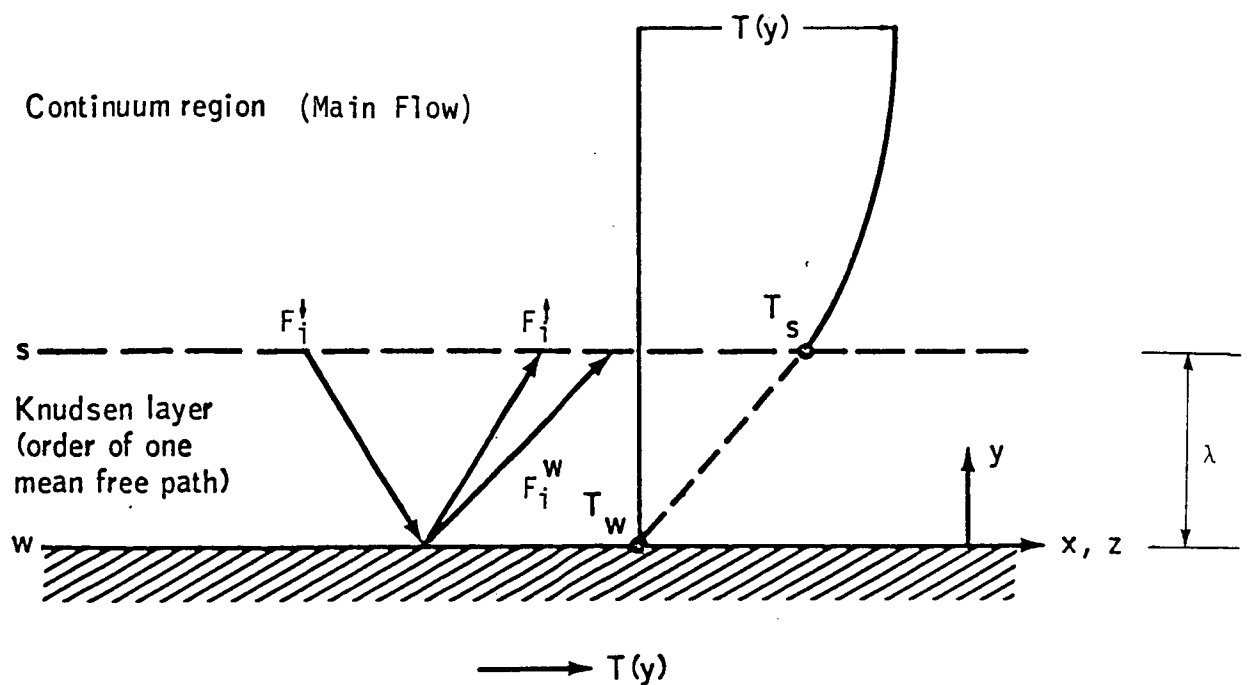


Figure 1. The Knudsen layer showing general fluxes and coordinate axes. The temperature as a function of normal distance is schematically overlayed.

$$k_{wA} = \left( \frac{2\gamma_A}{2-\gamma_A} \right) \sqrt{\frac{kT_w}{2\pi m_A}} \quad (69)$$

without slip and higher order shear.

For a noncatalytic wall (with  $\gamma_A = 0$ ), Eq. (49) gives

$$\left( \frac{\partial C_i}{\partial y} \right)_w = 0 \quad (70)$$

for all the species of a multicomponent mixture.

Binary Mixture. For a two-species mixture of atoms and molecules, Eq. (55b) gives

$$C_A^w = \frac{1}{k_{wA}} \times \left( D_{AM} \frac{\partial C_A}{\partial y} \right)_w \quad (71)$$

for a surface with finite catalycity and

$$\left( \frac{\partial C_A}{\partial y} \right)_w = 0 \quad (72)$$

for a noncatalytic surface. Eqs. (71) and (72) are employed in Ref. 4.

Appendices D and E give the slip and no-slip boundary conditions (presented in the text earlier), in the dimensionless form for the body-fitted and spherical polar coordinates, respectively, for a planar flow. The various integrals employed for evaluation the net, incident, and specularly reflected fluxes defined through Eqs. (5) to (7), respectively, are given in Appendix F.

## DISCUSSION AND CONCLUSIONS

The present analysis provides a consistent formulation for the slip equations for a multicomponent, binary, and single species mixture reacting catalytically on the surface. The differences between the slip expressions obtained by various researchers have been reconciled and implication of various assumptions (some of them inconsistent) contained in those expressions is discussed. The slip equations have also been obtained in body-fitted and spherical polar coordinates in a form which can readily be employed in the flow-field calculations.

Usually, the equation for pressure slip is not required as a boundary condition, but is needed to obtain the surface pressure. The temperature slip equation given here is for a constant surface temperature, which is provided as a boundary condition. For an adiabatic surface, however, the slip temperature,  $T_s$ , may be obtained by equating the wall heat-transfer rate to zero i.e.

$$q_w = \left( K \frac{\partial T}{\partial y} - \sum_{i=1}^{NS} j_i h_i + \mu v_{0x} \frac{\partial v_{0x}}{\partial y} \right)_s = 0$$

where the expression for mass flux  $j_i$  is provided in Appendix B and the higher order terms have been dropped. The temperature slip equation will now be required to obtain the wall temperature,  $T_w$ .

An expression has also been obtained for the finite-rate species-concentration boundary condition for a multicomponent gas mixture without surface slip. This boundary condition in the literature (Ref. 4) has generally been specified by assuming the dissociated air as a binary mixture.

However, the binary mixture formulation does not provide boundary conditions for the recombined molecules (on surface) such as  $O_2$  and  $N_2$  in a multicomponent mixture; it gives boundary conditions only for the recombining atoms.

To assess the importance of various terms in the general boundary conditions suggested here, a study is being undertaken in which the flow properties and boundary conditions would be varied systematically. The boundary equations form a simultaneous set, which is being coupled with a flow field calculation procedure in the stagnation region. These equations would finally be coupled with the viscous shock-layer code developed by Moss (Ref. 13) for the detailed flow-field calculations. The boundary equations obtained in the present work should provide a more realistic set of boundary conditions for a multi-component mixture for low-Reynolds-number slip flows as well as no-slip flows.

In conclusion, the boundary slip expressions obtained here are closed form solutions of the mass, momentum, and energy flux equations using the Chapman-Enskog velocity distribution function. This function represents a solution of the Boltzmann equation in the Navier-Stokes approximation.

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## APPENDIX A

### CONSTANTS APPEARING IN THE DISTRIBUTION FUNCTION AND DIFFUSION VELOCITY IN TERMS OF TRANSPORT PROPERTIES

The Sonine expansion coefficients  $a_{i0}$ ,  $a_{i1}$ ,  $b_{i0}$ , and  $c_{i0}^{(j)}$  appearing in the general velocity distribution function are found by a variational technique in which they are solutions to sets of simultaneous equations. References 2 and 7 provide the coefficients in terms of solutions to these set of equations. These solutions are expressed in terms of the collision integrals  $\Omega_{ij}^{(s,l)}$ . Reference 7 also provides the transport properties in terms of the Sonine expansion coefficients. Thus, in place of evaluating these coefficients in terms of the collision integrals, they may be expressed in terms of the transport properties. The various relations are:

(i) for  $a_{i0}$

$$D_i^T(\xi) = \frac{n_i m_i}{2} \sqrt{\frac{2kT}{m_i}} a_{i0}(\xi) \quad (A1)$$

(ii) for  $a_{i1}$

$$K(\xi) = -\frac{5}{4} k \sum_{i=1}^{NS} n_i \sqrt{\frac{2kT}{m_i}} a_{i1}(\xi) \quad (A2)$$

(iii) for  $b_{i0}$

$$\mu(\xi) = \frac{1}{2} kT \sum_{i=1}^{NS} n_i b_{i0}(\xi) \quad (A3)$$

(iv) for  $c_{i0}^{(j)}$

In the distribution function used here the Kernel  $\tilde{c}_i^{(j)} - \tilde{c}_i^{(k)}$

has associated Sonine polynomial coefficients  $c_i^{(j,k)}$ . Now  $\tilde{c}_i^{(i)} = 0$  (see Ref. 7), then  $c_{i0}^{(j)} \equiv c_{i0}^{(j,i)}$  and

$$D_{ij}(\xi) = \frac{\rho n_i}{2\bar{n} m_j} \sqrt{\frac{2kT}{m_i}} c_{i0}^{(j)}(\xi) \quad (A4)$$

where  $D_i^T(\xi)$ ,  $K(\xi)$ ,  $\mu(\xi)$ , and  $D_{ij}(\xi)$  are the multi-component thermal diffusion coefficient, thermal conductivity, coefficient of viscosity, and the multicomponent diffusion coefficient, respectively. The argument  $\xi$  is the number of terms used in the Sonine expansion. Except for  $D_i^T$ , letting  $\xi = 1$  gives quite good results for  $K$ ,  $\mu$  and  $D_{ij}$ . When  $\xi = 1$ , however, coefficients  $D_i^T$  vanish. Hence, in order to get the coefficient of thermal diffusion, it is necessary to take at least two terms in the Sonine expansion (i.e.  $\xi = 2$ ). If the argument does not appear with a coefficient (except for  $a_{i0}$ ), it is considered to have one term in the Sonine expansion.

The diffusion velocity for  $i$ th species in terms of the transport coefficients is obtained as (see ref. 7)

$$\bar{V}_k^i = \left( \frac{\bar{n}^2}{n_i \rho} \right) \sum_{j=1}^{NS} m_j D_{ij} d_k^j - \frac{1}{n_i m_i} D_i^T \frac{\partial \ln T}{\partial x_k} \quad (A5)$$

where the diffusion vector  $d_k^j$  for the  $j$ th species is defined after neglecting the external forces as (see Eq. (16) in the text):

$$d_k^j = \frac{\partial}{\partial x_k} \left( \frac{n_j}{\bar{n}} \right) + \left( \frac{n_j}{\bar{n}} - \frac{n_j m_j}{\rho} \right) \frac{\partial}{\partial x_k} (\ln p) \quad (A6)$$

Eq. (A6) may be simplified to obtain

$$d_k^j = \frac{\rho^2}{\bar{n}^2 m_j} \left[ \frac{1}{\bar{m}} \frac{\partial C_j}{\partial x_k} - C_j \sum_{q=1}^{NS} \left( \frac{1}{m_q} \frac{\partial C_q}{\partial x_k} \right) \right] \quad (A7)$$

#### SIMPLIFIED EXPRESSIONS FOR COEFFICIENTS $a_{i1}$ AND $b_{i0}$

Since  $a_{i1}$  and  $b_{i0}$  can not be obtained directly from equations (A2) and (A3), we introduce the following assumptions for the mixture thermal conductivity and viscosity; respectively,

$$K \approx \sum_{i=1}^{NS} \frac{n_i}{\bar{n}} K_i \quad (A8)$$

$$\mu \approx \sum_{i=1}^{NS} \frac{n_i}{\bar{n}} \mu_i \quad (A9)$$

Equations (A8) and (A9) are approximate forms for the more exact formula of Wilke (see ref. 14). These equations imply that

$$\sum_{j=1}^{NS} \frac{n_j}{\bar{n}} \phi_{ij} \approx 1 \quad (A10)$$

in the Wilke's relation. This is approximately true for air.

Thus, with the help of Eqs. (A2), (A3), (A8), and (A9) we may obtain the following approximate expressions for  $a_{i1}$  and  $b_{i0}$ , respectively,

$$n_i a_{i1} \approx -\frac{4}{5} \frac{n_i}{\bar{n}} \frac{K_i}{k} \sqrt{\frac{m_i}{2kT}} \quad (A11)$$

$$n_i b_{i0} \approx \frac{2}{kT} \frac{n_i}{\bar{n}} \mu_i \quad (A12)$$

For accurate evaluations of  $a_{i1}$  and  $b_{i0}$ , cumbersome expressions of the type of Eq. (7.4-49) of ref. 7 are required to be solved.

## APPENDIX B

### EVALUATED EXPRESSIONS FOR THE FLUXES OF MASS, MOMENTUM, AND ENERGY FROM INTEGRALS OVER THE DISTRIBUTION FUNCTION

The fluxes of mass, momentum, and energy (i.e. of a property  $\phi(\vec{V})$ ) are given in terms of integrals over the velocity distribution function  $f(\vec{V})$  in the "Analysis" section of main text. Here we give evaluated forms for these fluxes obtained from integration over the distribution functions. The various integrals needed in these evaluations are provided in Appendix F.

#### (i) Expressions for Mass Flux of Species

Net

$$M_{ik} = \frac{m_i n_i^s}{2} \left( \frac{2kT_s}{m_i} \right)^{1/2} \left[ - \left\{ \frac{\partial}{\partial x_k} (\ln T) \right\} a_{i0} + n \sum_{j=1}^{NS} c_{i0}^{(j)} d_k^j \right]_s ;$$

$$k = x, y, z \quad (B1)$$

Incident

$$\begin{aligned} M_i^\uparrow = & - \frac{m_i n_i^s}{2 \sqrt{\pi}} \left( \frac{2kT_s}{m_i} \right)^{1/2} \left[ 1 + \frac{b_{i0}}{6} \left( \frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right) \right]_s \\ & + \frac{1}{2} M_{iy} \end{aligned} \quad (B2)$$

Specularly Reflected

$$M_i^\uparrow = - M_i^\downarrow \quad (B3)$$

Diffusely Reflected

$$M_i^W = \frac{m_i n_i^W}{2\sqrt{\pi}} \left( \frac{2kT_w}{m_i} \right)^{1/2} \quad (B4)$$

It may be mentioned that  $M_{iy}$  as obtained here is similar to the mass flux ( $j_i$ ) expression of Ref. 14.

(ii) Correlation with Blottner's Expression (Ref. 15) for Mass Flux

If the thermal diffusion term is neglected in Eq. (B1) and substitutions are made for  $c_{i0}^{(j)}$  and  $d_k^j$  from Eqs. (A4) and (A7), Eq. (B1) may be simplified to obtain<sup>†</sup>

$$j_i \equiv M_{iy} = \frac{\rho W_i}{\bar{W}} \sum_{j \neq i}^{NS} D_{ij} \left[ \frac{\partial C_j}{\partial y} - C_j \bar{W} \sum_{q=1}^{NS} \frac{1}{W_q} \frac{\partial C_q}{\partial y} \right] \quad (B5)$$

where  $W_i$  is the molecular (or atomic) weight of the  $i$ th species and is related to the mass of the  $i$ th species,  $m_i$ , through the relation

$$\frac{m_i}{W_i} = \frac{k}{R} \quad (B6)$$

Here  $k$  is the Boltzmann constant and  $R$  is the universal gas constant. Equation (B5) may also be written as

$$j_i = \rho \frac{W_i}{\bar{W}} \sum_{j=1}^{NS} \left[ D_{ij} - \frac{\bar{W}}{W_j} \sum_{q \neq i}^{NS} D_{iq} C_q \right] \left( \frac{\partial C_j}{\partial y} \right) \quad (B7a)$$

or, with the introduction of the multicomponent Lewis number,  $L_{ij}$ , defined

<sup>†</sup>It may be noted here that  $D_{ii} = 0$ . See reference 7 for details.

as

$$L_{ij} = \rho C_p D_{ij} / K = \rho Pr D_{ij} / \mu,$$

Eq. (B7a) may be rewritten as

$$j_i = \frac{\mu}{Pr} \sum_{j=1}^{NS} \left[ \frac{W_i}{\bar{W}} L_{ij} - \frac{W_i}{W_j} \sum_{q \neq i}^{NS} L_{iq} C_q \right] \left( \frac{\partial C_j}{\partial y} \right) \quad (B7b)$$

or,

$$j_i = \frac{\mu}{Pr} \sum_{j \neq i}^{NS} \left[ \frac{W_i}{\bar{W}} L_{ij} + \left( 1 - \frac{W_i}{W_j} \right) \sum_{q \neq i}^{NS} L_{iq} C_q \right] \left( \frac{\partial C_j}{\partial y} \right) \quad (B7c)$$

or,

$$j_i = - \left( \frac{\mu}{Pr} \right) \left( Le_i \frac{\partial C_i}{\partial y} + \sum_{j \neq i}^{NS} \left\{ Le_i - \left[ \frac{W_i}{\bar{W}} L_{ij} + \left( 1 - \frac{W_i}{W_j} \right) \sum_{q \neq i}^{NS} L_{iq} C_q \right] \right\} \right. \\ \left. \times \frac{\partial C_j}{\partial y} \right) \quad (B7d)$$

or,

$$j_i = - \left( \frac{\mu}{Pr} \right) \left( Le_i \frac{\partial C_i}{\partial y} + \sum_{j \neq i}^{NS} \bar{\Delta} b_{ij} \frac{\partial C_j}{\partial y} \right) \quad (B7e)$$

where

$$\bar{\Delta} b_{ij} = Le_i - \left[ \frac{W_i}{\bar{W}} L_{ij} + \left( 1 - \frac{W_i}{W_j} \right) \sum_{q \neq i}^{NS} L_{iq} C_q \right] \quad (B8)$$

In general<sup>§</sup>,

$$L_{ij} = L_{ij} (C_i, M_i, M_j, L_{ij})$$

<sup>§</sup>See Eqs. (7), (8a), and (8b) of reference 15.

If the binary Lewis numbers  $L_{ij}$  are assumed to be the same for all the species, then

$$L_{ij} = L_{ij}^* = L_{ij}^*(C_i, M_i, M_j)$$

and Eq. (B8) for  $\bar{\Delta}b_{ij}$  becomes

$$\bar{\Delta}b_{ij}^* = Le_i - \left[ \frac{W_i}{\bar{W}} L_{ij}^* + \left( 1 - \frac{W_i}{W_j} \right) \sum_{q \neq i}^{NS} L_{iq}^* C_q \right] \quad (B9)$$

and the mass flux Eq. (B7e) now becomes

$$j_i = - \left( \frac{\mu}{Pr} \right) \left( Le_i \frac{\partial C_i}{\partial y} + \sum_{j \neq i}^{NS} \bar{\Delta}b_{ij}^* \frac{\partial C_j}{\partial y} \right) \quad (B10)$$

Further, if the binary Lewis numbers,  $L_{ij}$ , are constant for all the species, the term

$$\sum_{j \neq i}^{NS} \bar{\Delta}b_{ij}^* \frac{\partial C_j}{\partial y}$$

is zero in Eq. (B10). Therefore,

$$\sum_{j \neq i}^{NS} Le_i \frac{\partial C_j}{\partial y} = \sum_{j \neq i}^{NS} \left[ \frac{W_i}{\bar{W}} L_{ij}^* + \left( 1 - \frac{W_i}{W_j} \right) \sum_{q \neq i}^{NS} L_{iq}^* C_q \right] \left( \frac{\partial C_j}{\partial y} \right) \quad (B11a)$$



$$\text{or, } Le_i = - \frac{\sum_{j \neq i}^{NS} \frac{W_i}{\bar{W}} L_{ij}^* + (1 - \frac{W_i}{W_j}) \sum_{q \neq i}^{NS} L_{iq}^* C_q \left( \frac{\partial C_j}{\partial y} \right)}{\left( \frac{\partial C_i}{\partial y} \right)} \quad (B11b)$$

Thus, Eq. (B10) gives the mass flux due to concentration gradients only with  $\Delta b_{ij}^*$  and  $Le_i$  defined through Eqs. (B9) and (B11b), respectively.

To utilize Eqs. (B9) and (B11b),  $L_{ij}^*$  are still to be evaluated through complex matrix inversions (ref. 15). If we now make a little stronger assumption such that  $L_{ij}^* = L_{12}^* = Le$  (same for all the species), we obtain a much simpler expression for  $\Delta b_{ij}^*$  and Eq. (B11b) becomes

$$Le_i = Le \left[ \frac{W_i}{\bar{W}} - (1 - C_i) \left( \frac{\partial C_i}{\partial y} \right)^{-1} \sum_{j \neq i}^{NS} \left\{ \left( 1 - \frac{W_i}{W_j} \right) \frac{\partial C_j}{\partial y} \right\} \right] \quad (B12a)$$

or,

$$Le_i = Le \left[ \frac{W_i}{\bar{W}} + (1 - C_i) \left( \frac{\partial C_i}{\partial y} \right)^{-1} \sum_{j=1}^{NS} \left( \frac{W_i}{W_j} \right) \frac{\partial C_j}{\partial y} \right] \quad (B12b)$$

Similarly the expression for  $\bar{\Delta b}_{ij}^*$  may be obtained from Eq. (B9) as

$$\bar{\Delta b}_{ij}^* = Le_i - Le \left[ \frac{W_i}{\bar{W}} + \left( 1 - \frac{W_i}{W_j} \right) (1 - C_i) \right] \quad (B13)$$

It may be noted that for the case when  $\frac{\partial C_i}{\partial y} = 0$ , the term  $Le_i \frac{\partial C_i}{\partial y}$  in Eq. (B10) vanishes and Eq. (B12b) is not required. Further, employing a constant value for the Lewis number,  $Le (= \rho Pr D_{12}/\mu)$ , does not imply  $Le_i$  to have a constant value.

It should be pointed out here that for the case when  $L_{ij}$  is the same

for all the species we have used the condition

$$\sum_{j \neq i}^{NS} \bar{\Delta} b_{ik}^* \frac{\partial C_j}{\partial y} = 0$$

(and not just  $\bar{\Delta} b_{ik}^* = 0$  as employed in ref. 15) to obtain Eq. (B11b) for  $Le_i$ . The present formulation appears to provide a more consistent expression for  $Le_i$ .

Finally, Eqs. (B10), (B12b), and (B13) for a binary (two species) mixture give

$$j_i = - \frac{\mu}{Pr} Le \left( \frac{\partial C_i}{\partial y} \right); \text{ (Fick's law for mass flux)} \quad (B14)$$

$$Le_i = Le \quad (B15)$$

$$\bar{\Delta} b_{ij}^* = 0 \quad (B16)$$

(iii) Expressions For Normal Momentum Flux

Net

$$p_{iy} = p_i^s \left[ 1 + \frac{b_{i0}}{3} \left( \frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right) \right]_s \quad (B17a)$$

$$= p_i^s [1 + \tau_{yy}]_s \quad (B17b)$$

where  $\tau_{kl}^i$  are terms in the stress tensor for the  $i$ th species.

Incident and Specularly Reflected

$$p_{iy}^{\dagger} = p_{iy}^{\dagger} = p_i^s \left[ \frac{1}{2} + \frac{b_{i0}}{6} \left( \frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right) \right. \\ \left. + \frac{1}{\sqrt{\pi}} \frac{\partial \ell n T}{\partial y} \left( a_{i0} - \frac{1}{2} a_{i1} \right) - \frac{\bar{n}}{\sqrt{\pi}} \sum_{j=1}^{NS} c_{i0}^{(j)} d_y^j \right]_s \quad (B18)$$

Diffusely Reflected

$$p_{iy}^w = \frac{1}{2} p_i^w \quad (B19)$$

(iv) Expressions For Tangential Momentum Flux

Net

$$p_{ix} = - p_i^s \left[ \frac{b_{i0}}{2} \left( \frac{\partial v_{0x}}{\partial y} + \frac{\partial v_{0y}}{\partial x} \right) \right]_s \quad (B20)$$

$$p_{iz} = - p_i^s \left[ \frac{b_{i0}}{2} \left( \frac{\partial v_{0z}}{\partial y} + \frac{\partial v_{0y}}{\partial z} \right) \right]_s \quad (B21)$$

Incident and Specularly Reflected

$$p_{ix}^{\dagger} = - p_{ix}^{\dagger} = \frac{1}{\sqrt{\pi}} p_i^s \left[ - w_{0x} - \sqrt{\pi} \frac{b_{i0}}{4} \left( \frac{\partial v_{0x}}{\partial y} + \frac{\partial v_{0y}}{\partial x} \right) \right. \\ \left. + \frac{1}{2} \frac{\partial \ell n T}{\partial x} \left( a_{i0} - \frac{1}{2} a_{i1} \right) - \frac{\bar{n}}{2} \sum_{j=1}^{NS} c_{i0}^{(j)} d_x^j \right]_s \quad (B22)$$

$$p_{iz}^{\dagger} = - p_{iz}^{\dagger} = \frac{1}{\sqrt{\pi}} p_i^s \left[ - w_{0z} - \sqrt{\pi} \frac{b_{i0}}{4} \left( \frac{\partial v_{0z}}{\partial y} + \frac{\partial v_{0y}}{\partial z} \right) \right]$$

$$+ \frac{1}{2} \frac{\partial \ln T}{\partial z} \left( a_{i0} - \frac{1}{2} a_{i0} \right) - \frac{\bar{n}}{2} \sum_{j=1}^{NS} c_{i0}^{(j)} d_z^j \Big|_s \quad (B23)$$

Diffusely Reflected

$$p_{ix}^w = p_{iz}^w = 0 \quad (B24)$$

(v) Expressions For the Energy Flux

Net

$$E_{ik} = \frac{5}{4} \left( \frac{2kT_s}{m_i} \right) \left[ \frac{m_i n_i}{2} \left( \frac{2kT}{m_i} \right)^{1/2} \frac{\partial \ln T}{\partial x_k} a_{i1} + M_{ik} \right]_s ; k = x, y, z \quad (B25a)$$

$$= \dot{q}_{ik} + \frac{5}{2} \left( \frac{kT_s}{m_i} \right) M_{ik} ; \dot{q}_{ik} = - \left[ \frac{n_i K_i}{\bar{n}} \frac{\partial T}{\partial x_k} \right]_s \quad (B25b)$$

Incident and Specularly Reflected

$$E_i^\uparrow = - E_i^\downarrow = - \frac{m_i n_i^s}{2\sqrt{\pi}} \left( \frac{2kT_s}{m_i} \right)^{3/2} \left\{ 1 + \frac{b_{i0}}{4} \left( \frac{\partial v_{0x}}{\partial x} + \frac{\partial v_{0z}}{\partial z} - 2 \frac{\partial v_{0y}}{\partial y} \right) \right\}_s$$

$$+ \frac{1}{2} E_{iy} \quad (B26)$$

Diffusely Reflected

$$E_j^w = \frac{m_i n_i^w}{2 \sqrt{\pi}} \left( \frac{2kT_w}{m_i} \right)^{3/2} \quad (B27)$$

## APPENDIX C

### SLIP BOUNDARY CONDITIONS GIVEN BY DAVIS FOR A BINARY MIXTURE

In this appendix, the dimensional form of the slip boundary conditions obtained by Davis (Refs. 8 and 9) is provided for the purpose of comparison with the slip expressions obtained in the main text for a binary mixture.

The dimensionless form of the surface slip conditions provided in refs. 8 and 9 are

Concentration slip (ref. 8)<sup>†</sup>

$$C_A^S = C_{Ae} + \epsilon^2 \sqrt{\frac{\pi W_A}{2 \bar{W}}} \left( \frac{2 - \gamma_A}{\gamma_A} \right) \frac{(\bar{F}_D)_s}{\bar{p}_s} \sqrt{\frac{\bar{p}_s}{\bar{\rho}_s}} \left( \frac{\partial C_A}{\partial \bar{n}} \right)_s \quad (C1)$$

Velocity slip (ref. 8)

$$\bar{u}^S = \epsilon^2 a_1 \frac{\bar{\mu}_s}{\bar{p}_s} \sqrt{\frac{\bar{p}_s}{\bar{\rho}_s}} \left( \frac{\partial \bar{u}}{\partial \bar{n}} \right)_s \quad (C2)$$

Pressure slip (ref. 9)<sup>††</sup>

$$\bar{p}^S = \bar{p}_w + \epsilon^2 b_1 \frac{\bar{K}_s}{\bar{T}_s} \sqrt{\frac{\bar{p}_s}{\bar{\rho}_s}} \left( \frac{\partial \bar{T}}{\partial \bar{n}} \right)_s \quad (C3)$$

---

<sup>†</sup> Here the dimensionless quantities are denoted with a 'bar'. See Appendix D for details of nondimensionalization and the coordinate system.

<sup>††</sup> For the reasons explained in the main text, we have employed ' $\bar{K}$ ' in place of ' $\bar{\mu}$ ' in this expression.

Temperature slip (ref. 8)

$$\bar{T}_s = \bar{T}_w + \epsilon^2 c_1 \frac{\bar{k}_s}{\bar{p}} \sqrt{\frac{\bar{p}_s}{\bar{\rho}_s}} \left( \frac{\partial \bar{T}}{\partial \bar{n}} \right)_s \quad (C4)$$

With the help of the nondimensionalizing quantities given in refs. 8 and 9, the following dimensional forms of Eqs. (C1) through (C4) are obtained:

Concentration slip

$$C_A^s = C_{Ae}^s + \left( \frac{2-\gamma_A}{2\gamma_A} \right) \sqrt{\frac{2\pi m_A}{kT_s}} \left( D_{AM} \frac{\partial C_A}{\partial n^*} \right)_s \quad (C5)$$

Velocity slip

$$u^s = a_1 \frac{\mu_s}{\sqrt{kT_s}} \left( \frac{1}{\bar{n}\sqrt{\bar{m}}} \frac{\partial u}{\partial n^*} \right)_s \quad (C6)$$

Pressure slip

$$p = p_w + b_1 \left( \frac{\bar{\gamma}-1}{\bar{\gamma}} \right) \sqrt{\frac{\bar{m}}{kT_s}} \left( K \frac{\partial T}{\partial n^*} \right)_s \quad (C7)$$

Temperature slip

$$T = T_w + c_1 \left( \frac{\bar{\gamma}-1}{\bar{\gamma}} \right) \left[ \frac{K}{k} \frac{1}{\sqrt{kT}} \frac{\partial T}{\partial n^*} / \frac{\bar{n}}{\sqrt{\bar{m}}} \right]_s \quad (C8)$$

where  $n^*$  is the coordinate normal to surface (see Fig. D1 in Appendix D) and  $\bar{n}$  and  $\bar{m}$  are the number density and mass of a mixture molecule, respectively. The constants  $a_1$ ,  $b_1$ , and  $c_1$  are defined as:

$$a_1 = \left(\frac{5\pi}{16}\right) \sqrt{\frac{\pi}{2}} \left(\frac{2-\theta}{\theta}\right) = 1.2304 \left(\frac{2-\theta}{\theta}\right)$$

$$b_1 = \frac{15}{16} \sqrt{\frac{\pi}{2}} \left(\frac{2-\theta}{\theta}\right) = 1.1750 \left(\frac{2-\theta}{\theta}\right)$$

$$c_1 = \frac{75\pi}{128} \sqrt{\frac{\pi}{2}} \left(\frac{2-\theta}{\theta}\right) = 2.3071 \left(\frac{2-\theta}{\theta}\right)$$



## APPENDIX D

### SLIP CONDITIONS IN THE BODY-ORIENTED COORDINATE SYSTEM

In this Appendix we obtain the slip conditions for an axisymmetric body in the body-oriented coordinate  $(s^*, n^*)$  system. The coordinate configuration for such a system is given in Fig. D1. The equations of this Appendix contain simplifications similar to those given for a multicomponent mixture, following Eq. (38c) of the main text.

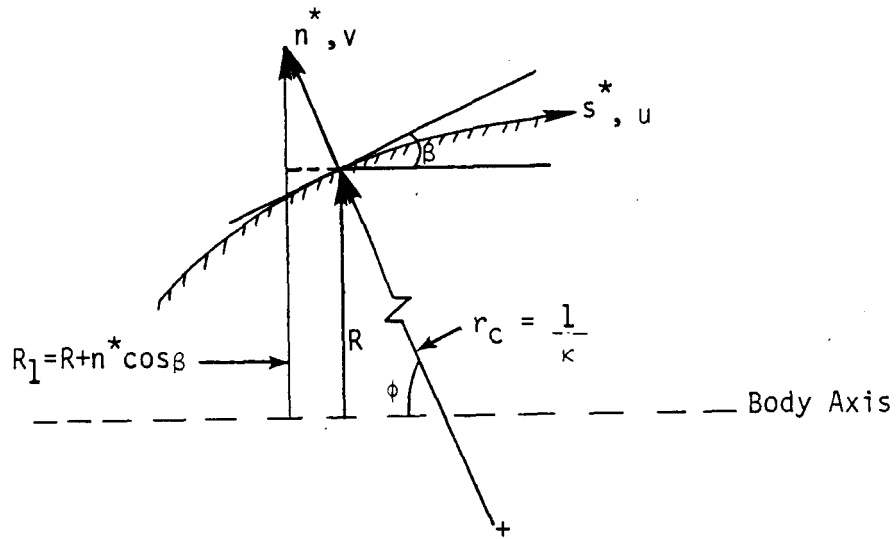


Figure D1. Coordinate Configuration For A Body (Symmetric About Its Axis)

By employing the metric coefficients (see ref. 16) of  $h_1 = 1 + n^* \kappa$  and  $h_2 = 1$ , equations (39) through (45) give the following slip equations in the body-oriented coordinate system.

Concentration slip

$$\frac{n_i^s}{n_i^w} = 2 \left[ 1 + \frac{1}{2} \frac{M_{iy}}{n_i^w m_i} \sqrt{\frac{2\pi m_i}{kT_w}} \sqrt{\frac{T_w}{T_s}} \right] / \left( \frac{p_y}{p_s} + 1 \right) \quad (D1)$$

where (from Eqs. (35a) through (35c)) we define  $M_{iy}$  as:

$$M_{Ay} = -k_{wA} n_A^w m_A \quad ; \quad A = O, N \quad (D2a)$$

$$M_{My} = k_{wA} n_A^w m_A \quad ; \quad \begin{cases} A = O \text{ for } M = O_2; \\ A = N \text{ for } M = N_2 \end{cases} \quad (D2b)$$

For all other atoms and molecules

$$M_{iy} = 0 \quad (D2c)$$

Pressure slip

$$\begin{aligned} p^s = & \left\{ -\frac{\theta}{3} \left[ \mu \left( \frac{1}{1+n^* \kappa} \frac{\partial u}{\partial s^*} - 2 \frac{\partial v}{\partial n^*} \right) \right]_s + \frac{2}{5} \left( \frac{2-\theta}{\sqrt{\pi}} \right) \left[ \frac{1}{\sqrt{2kT}} \frac{\partial T}{\partial n^*} \right. \right. \\ & \times \sum_{i=1}^{NS} \frac{n_i K_i}{\bar{n}} \sqrt{m_i} \left. \right]_s + \frac{\theta}{2} p^w \left. \right\} / \left\{ \frac{\theta}{2} - \frac{2(2-\theta)}{\sqrt{\pi}} \frac{D_{12}}{\sqrt{2kT_s}} \right. \\ & \times \sum_{i=1}^{NS} \sqrt{m_i} \left[ \frac{\partial C_i}{\partial n^*} + (1-C_i) \sum_q \left( \frac{\bar{m}}{m_q} \frac{\partial C_q}{\partial n^*} \right) \right]_s \left. \right\} \quad (D3) \end{aligned}$$

Velocity slip

$$u^s = \left\{ \sqrt{\frac{\pi}{2}} \left( \frac{2-\theta}{\theta} \right) \left[ \frac{\mu}{\sqrt{kT}} \left( \frac{\partial u}{\partial n^*} - \frac{\kappa u}{1+n^* \kappa} + \frac{1}{1+n^* \kappa} \frac{\partial v}{\partial s^*} \right) \right]_s \right.$$

$$\begin{aligned}
& + \frac{1}{5} \left[ \frac{1}{k T} \frac{1}{(1+n^* \kappa)} \frac{\partial T}{\partial s^*} \sum_{i=1}^{NS} \frac{n_i K_i}{\bar{n}} \sqrt{m_i} \right]_s \\
& + n_s D_{12}^s \sum_{i=1}^{NS} \sqrt{m_i} \left[ \frac{1}{(1+n^* \kappa)} \frac{\partial C_i}{\partial s^*} + (1-C_i) \sum_{q=1}^{NS} \frac{\bar{m}}{m_q} \frac{1}{(1+n^* \kappa)} \frac{\partial C_q}{\partial s^*} \right]_s \} \\
& / \sum_{i=1}^{NS} n_i^s \sqrt{m_i}
\end{aligned} \tag{D4}$$

Temperature slip

$$\begin{aligned}
\frac{T_s}{T_w} = & \left\{ - \frac{\sqrt{\pi}}{\bar{n}_s} \sum_{i=1}^{NS} \frac{M_{iy}}{m_i} - \frac{\sqrt{\pi}}{\bar{n}_s} \sum_i \frac{M_{iy}}{m_i} + \frac{1}{2} \left( \frac{p_y}{p^s} + 1 \right) \right. \\
& \text{diatomic} \\
& \text{molecules} \\
& \times \sum_i \sqrt{\frac{2kT_s}{m_i}} \left( \frac{\bar{m}_s}{m_i} \right) C_i^s + \frac{1}{2} \left( \frac{p_y}{p^s} + 1 \right) \sum_{i=1}^{NS} \sqrt{\frac{2kT_s}{m_i}} \left( \frac{\bar{m}_s}{m_i} \right) C_i^s \\
& \text{diatomic} \\
& \text{molecules} \\
& / \left[ - \sqrt{\pi} \left( \frac{2-\theta}{\theta} \right) \left\{ \frac{1}{2} \frac{K}{p} \frac{\partial T}{\partial n^*} - \frac{5}{4} \sum_{i=1}^{NS} \left( \frac{M_{iy}}{\bar{n} m_i} \right) \right. \right. \\
& - \frac{1}{\bar{n}} \sum_i \frac{M_{iy}}{m_i} \left. \right\}_s + \frac{1}{4} \left( 3 \frac{p_y}{p^s} + 1 \right) \sum_{i=1}^{NS} \sqrt{\frac{2kT_s}{m_i}} \left( \frac{\bar{m}_s}{m_i} \right) C_i^s \\
& \text{diatomic} \\
& \text{molecules} \\
& + \frac{1}{2} \left( \frac{p_y}{p^s} + 1 \right) \sum_i \sqrt{\frac{2kT_s}{m_i}} \left( \frac{\bar{m}_s}{m_i} \right) C_i^s \left. \right] \\
& \text{diatomic} \\
& \text{molecules}
\end{aligned} \tag{D5}$$

If the internal energy (comprising of rotational and vibrational energies in this case) is considered frozen during reflection from the surface, the following form of the temperature slip equation is obtained (see Eq. (28) of Ref. 5):

$$\begin{aligned}
 \frac{T_s}{T_w} = & \left\{ -\frac{\sqrt{\pi}}{\bar{n}_s} \sum_{i=1}^{NS} \frac{M_{iy}}{m_i} + \frac{1}{2} \left( \frac{p_y}{p^s} + 1 \right) \right. \\
 & \times \sum_{i=1}^{NS} \sqrt{\frac{2kT_s}{m_i}} \left( \frac{\bar{m}_s}{m_i} \right) C_i^s \} \\
 & / \left[ -\sqrt{\pi} \left( \frac{2-\theta}{\theta} \right) \left\{ \frac{1}{2} \left( \frac{K}{p} \frac{\partial T}{\partial n^*} \right)_s - \frac{5}{4} \sum_{i=1}^{NS} \left( \frac{M_{iy}}{\bar{n} m_i} \right)_s \right\} \right. \\
 & \left. + \frac{1}{4} \left( 3 \frac{p_y}{p^s} + 1 \right) \sum_{i=1}^{NS} \sqrt{\frac{2kT_s}{m_i}} \left( \frac{\bar{m}_s}{m_i} \right) C_i^s \right] \quad (D6)
 \end{aligned}$$

Equation for  $n_i^s$

$$n_i^s = \frac{p_s}{m_i} \left[ 1 + \frac{\left( \frac{\partial C_i}{\partial n^*} \right)_s + \frac{1}{\bar{m}_i} \left( \frac{\psi_i}{D_{12}} \right)_s}{\sum_{q=1}^{NS} \left( \frac{\bar{m}}{m_q} \frac{\partial C_q}{\partial n^*} \right)_s} \right] \quad (D7)$$

where

$$\psi_A^s = - \frac{\gamma_A}{(2-\gamma_A)} \frac{1}{\sqrt{\pi}} \frac{m_A n_A^s}{2\bar{n}_s} \sqrt{\frac{2kT_s}{m_A}} \left( \frac{p_{Ay}}{p_A^s} + 1 \right) ; \quad A = O, N \quad (D8a)$$

$$\psi_M^s = - \psi_A^s ; \quad \begin{cases} A = O \text{ for } M = O_2; \\ A = N \text{ for } M = N_2; \end{cases} \quad (D8b)$$

$$\psi_i^s = 0 \quad \text{for all other species} \quad (D8c)$$

In Eqs. (D1), (D5), (D6) and (D8a) the ratio  $\frac{p_y}{p^s}$  is defined as

$$\frac{p_y}{p^s} = \left[ 1 + \frac{b_0}{3} \left( \frac{1}{1+n^*} \frac{\partial u}{\partial s^*} - 2 \frac{\partial v}{\partial n^*} \right) \right]_s \quad (D9)$$

and  $b_0$  is related to viscosity,  $\mu$ , through the relation

$$\mu = \frac{1}{2} \bar{n} k T b_0 \quad (D10)$$

which has been obtained from (A3) by assuming  $b_{i0}$  to be the same ( $b_0$ ) for all the species.

Equations (D1) through (D8) may now be nondimensionalized by using the following relations (refs. 8 and 13):

$$\bar{u} = \frac{u}{U_\infty}, \quad \bar{v} = \frac{v}{U_\infty}, \quad \bar{T} = \frac{T}{U_\infty^2 / C_{p,\infty}} = \frac{T}{T_{ref}}$$

$$\bar{p} = \frac{p}{\rho_{\infty} U_{\infty}^2}, \quad \bar{\rho} = \frac{\rho}{\rho_{\infty}}, \quad \bar{\mu} = \frac{\mu}{\mu(T_{\text{ref}})} = \frac{\mu}{\mu_{\text{ref}}}$$

$$\bar{c}_p = \frac{c_p}{c_{p,\infty}}, \quad \bar{h} = \frac{h}{U_{\infty}^2}, \quad \bar{k}_{wi} = \frac{k_{wi}}{U_{\infty}}$$

$$\bar{K} = \frac{K}{c_{p,\infty} \mu_{\text{ref}}}, \quad \bar{s} = \frac{s^*}{r_N}, \quad \bar{n} = \frac{n^*}{r_N},$$

$$\bar{\kappa} = \kappa r_N, \quad \bar{R} = \frac{R}{r_N}, \quad \bar{M}_{iy} = \frac{M_{iy}}{n_i^w m_i U_{\infty}}$$

$$\bar{\psi}_i = \frac{\psi_i}{m_A D_{12}/r_N}, \quad \bar{k}_{wA} = \frac{k_{wA}}{U_{\infty}}$$

Introducing the nondimensional quantities as defined here, the following equations are obtained from Eqs. (D-1) through (D-8):

#### Concentration slip

$$\frac{C_i^s}{C_i^w} = 2 \frac{\bar{\rho}_w}{\bar{\rho}_s} \left[ 1 + \frac{1}{2} M_{\infty} \bar{M}_{iy} \sqrt{2\pi \bar{\gamma}_{\infty} \frac{W_i}{W_{\infty}} \frac{T_{\infty}}{T_w}} \right] \sqrt{\frac{\bar{T}_w}{\bar{T}_s}} / \left( \frac{p_y}{p^s} + 1 \right) \quad (\text{D11})$$

where

$$\bar{M}_{Ay} = -\bar{k}_{wA}; \quad A = 0, N \quad (\text{D12a})$$

$$\bar{M}_{My} = \bar{k}_{wA} \left( \frac{C_A^w}{C_M^w} \right); \begin{cases} A = O & \text{for } M = O_2; \\ A = N & \text{for } M = N_2; \end{cases} \quad (D12b)$$

$$\bar{M}_{iy} = 0 \text{ for all other atoms and molecules} \quad (D12c)$$

### Pressure slip

$$\begin{aligned} \bar{p}^s = & \left\{ \bar{p}_w - \epsilon^2 \left[ \frac{2}{3} \bar{\mu} \left( \frac{1}{1+\bar{n}} \frac{\partial \bar{u}}{\partial \bar{s}} - 2 \frac{\partial \bar{v}}{\partial \bar{n}} \right) \right]_s \right. \\ & + \epsilon^2 \left[ \frac{2}{5 \sqrt{\pi}} \left( \frac{2-\theta}{\theta} \right) \left( \frac{\bar{\gamma}}{\bar{\gamma}-1} \right)_s \left( \frac{1}{M_\infty Pr_s} \right) \sqrt{\frac{2 T_{ref} T_s \bar{W}_\infty}{\bar{\gamma}_\infty T_\infty \bar{W}_s}} \left( \frac{1}{\bar{T}} \frac{\partial \bar{T}}{\partial \bar{n}} \right)_s \right. \\ & \left. \left. \times \sum_{i=1}^{NS} \left( \frac{\bar{W}_s}{\bar{W}_i} \right)^{3/2} C_i^s \bar{\mu}_i^s \right] \right\} \\ & / \left\{ 1 - \frac{4}{\sqrt{\pi}} \left( \frac{2-\theta}{\theta} \right) \epsilon^2 \left( \frac{Le_s M_\infty}{Pr_s} \right) \sqrt{\frac{\bar{\gamma}_\infty T_\infty}{2 T_{ref} \bar{T}_s}} \left( \frac{\bar{\mu}_s}{\bar{\rho}_s} \right) \right. \\ & \left. \times \sum_{i=1}^{NS} \sqrt{\frac{\bar{W}_i}{\bar{W}_\infty}} \left[ \frac{\partial C_i}{\partial \bar{n}} + (1 - C_i) \sum_q \left( \frac{\bar{W}}{\bar{W}_q} \frac{\partial C_q}{\partial \bar{n}} \right) \right]_s \right\} \quad (D13) \end{aligned}$$

where we have assumed that  $Pr \approx Pr_i$  and  $C_{pi}/R_i = (\bar{\gamma} - 1)/\bar{\gamma}$

### Velocity Slip

$$\bar{u}^s = \epsilon^2 \left( \frac{M_\infty \bar{\mu}_s}{\bar{\rho}_s} \right) \left( \frac{1}{\sum_{i=1}^{NS} \sqrt{\frac{\bar{W}}{\bar{W}_i}} C_i} \right)_s \left[ \sqrt{\pi} \left( \frac{2-\theta}{\theta} \right) \sqrt{\frac{\bar{\gamma}_\infty T_\infty}{2 T_{ref} \bar{T}_s}} \right]$$

$$\begin{aligned}
& \times \left( \frac{\partial \bar{u}}{\partial \bar{n}} - \frac{\bar{\kappa} \bar{u}}{1+\bar{n}\bar{\kappa}} + \frac{1}{1+\bar{n}\bar{\kappa}} \frac{\partial \bar{v}}{\partial \bar{s}} \right)_s + \frac{1}{5} \frac{1}{M_\infty Pr_s} \left( \frac{\bar{\gamma}}{\bar{\gamma}-1} \right)_s \left( \frac{1}{\bar{T}} \frac{1}{(1+\bar{n}\bar{\kappa})} \frac{\partial T}{\partial \bar{s}} \right)_s \\
& \times \sum_{i=1}^{NS} \left( \frac{\bar{w}_i}{W_i} \right)^{3/2} C_i^s \frac{\bar{\mu}_i^s}{\bar{\mu}_s} + \frac{Le_s}{M_\infty Pr_s} \sum_{i=1}^{NS} \sqrt{\frac{W_i}{\bar{w}_s}} \left\{ \frac{1}{1+\bar{n}\bar{\kappa}} \frac{\partial C_i}{\partial \bar{s}} + (1-C_i) \sum_{q=1}^{NS} \left( \frac{\bar{w}_q}{W_q} \right) \frac{1}{(1+\bar{n}\bar{\kappa})} \left( \frac{\partial C_q}{\partial \bar{s}} \right) \right\}_s
\end{aligned}
\tag{D14}$$

Temperature Slip

$$\begin{aligned}
\frac{T_s}{T_w} = & \left\{ -\sqrt{\frac{\pi}{2}} \left( \frac{\bar{p}_w}{\bar{p}_s \bar{p}_s} \right) \left[ \sum_{i=1}^{NS} \bar{M}_{iy} C_i^w \left( \frac{\bar{w}_i}{W_i} \right) + \sum_i \bar{M}_{iy} C_i^w \left( \frac{\bar{w}_i}{W_i} \right) \right] \right. \\
& \text{diatomic molecules} \\
& + \frac{1}{2} \left( \frac{p_y}{p_s} + 1 \right) \left[ \sum_{i=1}^{NS} \left( \frac{\bar{w}_i}{W_i} \right)^{3/2} C_i^s + \sum_i \left( \frac{\bar{w}_i}{W_i} \right)^{3/2} C_i^s \right] \Big\} \\
& \text{diatomic molecules} \\
& / \left[ -\sqrt{\frac{\pi}{2}} \left( \frac{2-\theta}{\theta} \right) \left\{ \frac{\epsilon^2}{2\bar{\gamma}_\infty} \left( \frac{1}{M_\infty^2 Pr_s} \right) \left( \frac{\bar{u}}{\bar{p}} \right)_s \left( \frac{\bar{\gamma}}{\bar{\gamma}-1} \right)_s \left( \frac{T_{ref}}{T_\infty} \right) \sqrt{\frac{\bar{p}_s}{\bar{p}_s}} \right. \right. \\
& \times \left( \frac{\bar{w}_\infty}{W_s} \right) \left( \frac{\partial T}{\partial \bar{n}} \right)_s - \frac{5}{4} \left( \frac{\bar{p}_w}{\sqrt{\bar{p}_s \bar{p}_s}} \right) \sum_{i=1}^{NS} \bar{M}_{iy} C_i^w \left( \frac{\bar{w}_i}{W_i} \right) \\
& \left. \left. - \left( \frac{\bar{p}_w}{\sqrt{\bar{p}_s \bar{p}_s}} \right) \sum_i \bar{M}_{iy} C_i^w \left( \frac{\bar{w}_i}{W_i} \right) \right\} + \frac{1}{4} \left( 3 \frac{p_y}{p_s} + 1 \right) \sum_{i=1}^{NS} \left( \frac{\bar{w}_i}{W_i} \right)^{3/2} C_i^s \right. \\
& \left. \text{diatomic molecules} \right]
\end{aligned}$$



$$+ \frac{1}{2} \left( \frac{p}{p_s} y + 1 \right) \sum_{\substack{i \\ \text{diatomic} \\ \text{molecules}}} \left( \frac{W_s}{W_i} \right)^{3/2} C_i^s \quad (D15)$$

Or, with frozen internal energy during reflection from surface,

$$\begin{aligned} \frac{T_s}{T_w} = & \left\{ -\sqrt{\frac{\pi}{2}} \frac{\left( \frac{\bar{p}_w}{\bar{p}_s \bar{p}_s} \right)}{\sqrt{\bar{p}_s \bar{p}_s}} \sum_{i=1}^{NS} \bar{M}_{iy} C_i^w \left( \frac{\bar{W}_s}{W_i} \right) + \frac{1}{2} \left( \frac{p}{p_s} y + 1 \right) \sum_{i=1}^{NS} \left( \frac{\bar{W}_s}{W_i} \right)^{3/2} C_i^s \right\} \\ & / \left[ -\sqrt{\frac{\pi}{2}} \frac{(2-\theta)}{\theta} \left\{ \frac{\epsilon^2}{2\bar{\gamma}_\infty} \left( \frac{1}{M_\infty^2 Pr_s} \right) \left( \frac{\bar{\mu}}{\bar{p}} \right)_s \left( \frac{\bar{\gamma}}{\bar{\gamma}-1} \right)_s \left( \frac{T_{ref}}{T_\infty} \right) \sqrt{\frac{\bar{p}_s}{\bar{p}_s}} \right. \right. \\ & \times \left. \left( \frac{\bar{W}_\infty}{\bar{W}_s} \right) \left( \frac{\partial T}{\partial \bar{n}} \right)_s - \frac{5}{4} \left( \frac{\bar{p}_w}{\bar{p}_s \bar{p}_s} \right) \sum_{i=1}^{NS} \bar{M}_{iy} C_i^w \left( \frac{\bar{W}_s}{W_i} \right) \right\} \\ & + \frac{1}{4} \left( 3 \frac{p}{p_s} y + 1 \right) \sum_{i=1}^{NS} \left( \frac{\bar{W}_s}{W_i} \right)^{3/2} C_i^s \quad (D16) \end{aligned}$$

Equation for  $n_i^s$

$$C_i^s = \frac{n_{i,m}^s}{\rho_s} = 1 + \frac{\left\{ \frac{\partial C_i}{\partial \bar{n}} + \frac{W_A}{W_i} \bar{\psi}_i \right\}_s}{\sum_{q=1}^{NS} \left( \frac{\bar{W}}{W_q} \frac{\partial C_q}{\partial \bar{n}} \right)_s} ; \quad \begin{cases} A = 0 & \text{for } i=O_2; \\ A = N & \text{for } i=N_2; \end{cases} \quad (D17)$$

where

$$\begin{aligned} \bar{\psi}_A^s = \frac{r_{N A}^s}{m_A D_{12}^s} = - \frac{\gamma_A}{(2-\gamma_A)} \left( \frac{1}{\epsilon^2 M_\infty} \right) \sqrt{\frac{\bar{W}_\infty T_s}{2\pi \bar{\gamma}_\infty W_A T_\infty}} \left( \frac{\bar{W}_s}{W_A} \right) \left( \frac{Pr}{Le} \right)_s \left( \frac{\bar{\rho}}{\bar{\mu}} \right)_s \\ \times \left( \frac{p_y}{p^s} + 1 \right) C_A^s ; A = O, N \end{aligned} \quad (D18a)$$

$$\bar{\psi}_M^s = -\bar{\psi}_A^s ; \begin{cases} A = O & \text{for } M = O_2 \\ A = N & \text{for } M = N_2 \end{cases} \quad (D18b)$$

$$\bar{\psi}_i^s = 0 \text{ for all other species} \quad (D18c)$$

and

$$\begin{aligned} \frac{p_y}{p^s} = \frac{\bar{p}_y}{\bar{p}^s} = \left[ 1 + \frac{2}{3} \left( \frac{\bar{\gamma}_\infty T_\infty}{T_{ref}} \right) \left( \frac{\bar{\mu}}{\bar{\rho} T} \right)_s \epsilon^2 M_\infty^2 \frac{\bar{W}_s}{\bar{W}_\infty} \right. \\ \left. \times \left( \frac{1}{1 + \bar{n} \bar{\kappa}} \frac{\partial \bar{u}}{\partial \bar{s}} - 2 \frac{\partial \bar{v}}{\partial \bar{n}} \right)_s \right] \end{aligned} \quad (D19)$$

or,

$$\frac{p_y}{p^s} = 1 + \frac{2}{3} \frac{\bar{\mu}_s}{\bar{p}_s} \epsilon^2 \left( \frac{1}{1 + \bar{n} \bar{\kappa}} \frac{\partial \bar{u}}{\partial \bar{s}} - 2 \frac{\partial \bar{v}}{\partial \bar{n}} \right)_s$$

$$W_i = m_i R/k$$

$$\epsilon^2 = \frac{\mu_{ref}}{\rho_\infty U_\infty r_N} \quad (\text{Reynolds number parameter})$$

$$Pr = \frac{C_p \mu}{K} \quad (\text{Prandtl number})$$

$$Le = \frac{\rho C_p D_{12}}{K} \quad (\text{Lewis number})$$

$$M_\infty = \frac{U_\infty}{a_\infty} \quad (\text{Mach number})$$

and

$$\bar{k}_{wA} = \frac{\gamma_A}{M_\infty} \sqrt{\frac{\bar{W}_\infty \bar{T}_s T_{ref}}{2\pi \bar{Y}_\infty W_A T_\infty}} \sqrt{\frac{T_w}{\bar{T}_s T_{ref}}} \quad (\text{Recombination rate constant})$$

For a noncatalytic surface ( $\gamma_A = \bar{k}_{wA} = 0$ ), eq. (D18a) through (D18c) give  $\bar{\psi}_i^s = 0$  for all species. For this case, Eq. (D17) becomes

$$\left(\frac{\partial C_i}{\partial \bar{n}}\right)_s = - (1 - C_i^s) \sum_{q=1}^{NS} \left(\frac{\bar{W}_s}{W_q} \frac{\partial C_q}{\partial \bar{n}}\right)_s \quad (D20)$$

Equation (D20), similar to Eq. (47b), gives

$$\left(\frac{\partial C_i}{\partial \bar{n}}\right)_s = 0 \quad (D21)$$

which may be employed as the boundary condition for a noncatalytic surface with a multicomponent gas mixture (with the binary assumption for diffusion

coefficients). For a fully catalytic surface, employing  $\gamma_A = 1$  and using Eqs. (D18a) through (D18c) in Eq. (D17) would yield the appropriate concentration slip.

If the multicomponent diffusion coefficients are retained without the binary assumption the underlined terms in Eq. (D13) are to be replaced by

$$- \sum_{\substack{j=1 \\ j \neq i}}^{NS} \frac{L_{ij}}{Le} \left[ \frac{\partial C_j}{\partial \bar{n}} - C_j \sum_{q=1}^{NS} \frac{\bar{W}}{W_q} \frac{\partial C_q}{\partial \bar{n}} \right]_s$$

and the underlined term in Eq. (D14) are to be replaced by

$$- \sum_{\substack{j=1 \\ j \neq i}}^{NS} \frac{L_{ij}}{Le} \left\{ \frac{1}{(1+\bar{n}\kappa)} \frac{\partial C_j}{\partial \bar{s}} - C_j \sum_{q=1}^{NS} \left( \frac{\bar{W}}{W_q} \frac{1}{(1+\bar{n}\kappa)} \frac{\partial C_q}{\partial \bar{s}} \right) \right\}_s$$

where the multicomponent Lewis number,  $L_{ij}$ , is defined as

$$L_{ij} = \frac{\rho C_p D_{ij}}{K}$$

#### Simplifications For A Binary Mixture

When all the species in a gas mixture can be considered as atoms and molecules only (see ref. 8), Eqs. (D11) through (D18) may be further simplified. With the assumption of  $p_y/p^s \approx 1$ , Eqs. (D11) through (D18) for a binary mixture yield:

Concentration Slip

$$\frac{C_A^S}{C_A^W} = \frac{\bar{\rho}_W}{\bar{\rho}_S} \left( \frac{2-\gamma_A}{2} \right) \sqrt{\frac{\bar{T}_W}{\bar{T}_S}} \quad (D22)$$

Pressure Slip

$$\bar{p}^S = \bar{p}_W + \frac{4}{5\sqrt{2\pi}} \left( \frac{\bar{\gamma}}{\bar{\gamma}-1} \right)_S \left( \frac{2-\theta}{\theta} \right) \frac{\epsilon^2}{Pr} \frac{1}{\bar{T}_S} \sqrt{\frac{\bar{p}_S}{\bar{\rho}_S}} \left( \frac{\partial \bar{T}}{\partial \bar{n}} \right)_S$$

$$\times \left( \frac{\bar{W}_S}{W_A} \right)^{3/2} \left[ C_A^S \bar{\mu}_A^S + \left( \frac{W_A}{W_M} \right)^{3/2} (1 - C_A^S) \bar{\mu}_M^S \right] \quad (D23)$$

where we have used the equation of state

$$\frac{\bar{p}_S}{\bar{\rho}_S} = \frac{1}{M_\infty^2} \left( \frac{\bar{T}_S T_{ref}}{\bar{\gamma}_\infty T_\infty} \right) \frac{\bar{W}_\infty}{\bar{W}_S} \quad (D24)$$

and neglected the higher order shear terms as well as diffusion terms.

Velocity slip

$$\bar{u}^S = \sqrt{\frac{\pi}{2}} \left( \frac{2-\theta}{\theta} \right) \epsilon^2 \frac{\bar{\mu}_S}{\sqrt{\bar{p}_S \bar{\rho}_S}} \sqrt{\frac{\bar{W}_\infty}{\bar{W}_S}} \left( \frac{\partial \bar{u}}{\partial \bar{n}} - \frac{\bar{\kappa} \bar{u}}{1+\bar{n} \bar{\kappa}} \right) \quad (D25)$$

where we have again employed the equation of state given earlier and neglected higher order shear, conduction, and diffusion terms. In obtaining Eq. (D25) we have also used the approximation:

$$x = \frac{[C_A^S (W_M - W_A) - W_A]^{1/2}}{[C_A^S (\sqrt{W_M} - \sqrt{W_A}) + \sqrt{W_A}]} \approx 1$$

To be more exact one may keep this factor in Eq. (D25).

Temperature slip

$$\begin{aligned} \bar{T}_s = [ \bar{T}_w + \frac{1}{2} \sqrt{\frac{\pi}{2}} x_1 \left( \frac{\bar{\gamma}}{\bar{\gamma}-1} \right)_s \left( \frac{2-\theta}{\theta} \right) \left( \frac{\epsilon^2}{Pr_s} \right) \frac{\bar{\mu}_s}{\sqrt{\bar{p}_s \bar{\rho}_s}} \left( \frac{\partial \bar{T}}{\partial n} \right)_s ] \\ / \left\{ 1 - \frac{1}{4} \sqrt{\frac{\pi}{2}} \left( \frac{2-\theta}{\theta} \right) x_1 \frac{\bar{\rho}_w \bar{k}_{wA}}{\sqrt{\bar{p}_s \bar{\rho}_s}} \frac{C_A^w}{(C_A^S + 1)} \right\} \end{aligned} \quad (D26)$$

where

$$x_1 = \frac{[C_A(W_M - W_A) + W_A]^{3/2}}{[C_A(W_M^{3/2} - 2 W_A^{3/2}) + 2 W_A^{3/2}]}$$

and  $\frac{1}{2} < x_1 < 1$  for  $0 < C_A < 1$  and diatomic molecules ( $W_M = 2 W_A$ ). In obtaining Eq. (D26), we have employed the equation of state and  $W_M = 2 W_A$ .

With frozen internal energy during reflection from the surface, the temperature slip equation becomes

$$\begin{aligned}
T_s = & \left[ T_w + \frac{1}{2} \sqrt{\frac{\pi}{2}} x_2 \left( \frac{\bar{\gamma}}{\bar{\gamma}-1} \right)_s \left( \frac{2-\theta}{\theta} \right) \frac{\epsilon^2}{Pr_s} \frac{\bar{\mu}_s}{\sqrt{\bar{p}_s \bar{\rho}_s}} \left( \frac{\partial \bar{T}}{\partial \bar{n}} \right)_s \right. \\
& \left. + \sqrt{\frac{\pi}{2}} x_2 \frac{\bar{\rho}_w \bar{k}_{wA}}{\sqrt{\bar{p}_s \bar{\rho}_s}} \left\{ \frac{C_A^w}{(C_A^s + 1)} \right\} \bar{T}_w \right] \\
& / \left[ 1 - \frac{5}{4} \sqrt{\frac{\pi}{2}} x_2 \left( \frac{2-\theta}{\theta} \right) \frac{\bar{k}_{wA} \bar{\rho}_w}{\sqrt{\bar{p}_s \bar{\rho}_s}} \left\{ \frac{C_A^w}{(C_A^s + 1)} \right\} \right]
\end{aligned} \tag{D27}$$

where

$$x_2 = \frac{[C_A(W_M - W_A) + W_A]^{3/2}}{[C_A(W_M^{3/2} - W_A^{3/2}) + W_A^{3/2}]}$$

For diatomic molecules ( $W_M = 2 W_A$ ),  $x_2$  may be taken as unity for  $0 < C_A < 1$ . Equation (D27) employs  $W_M = 2W_A$ .

Equation for  $C_A^s$

$$C_A^s = \left( \frac{2-\gamma_A}{2} \right) \left( \frac{\epsilon^2}{\bar{k}_{wA}} \right) \left( \frac{Le}{Pr} \right)_s \left( \frac{\bar{\mu}}{\bar{\rho}} \right)_s \sqrt{\frac{T_w}{T_s T_{ref}}} \left( \frac{\partial C_A}{\partial \bar{n}} \right)_s \tag{D28}$$

Equation (28), for a noncatalytic surface with  $\gamma_A = \bar{k}_{wA} = 0$ , gives

$$\left( \frac{\partial C_A}{\partial \bar{n}} \right)_s = 0 \tag{D29}$$

whereas using  $\gamma_A = 1$  in Eq. (D29) and in the expression for  $\bar{k}_{WA}$ :

$$\bar{k}_{WA} = \frac{\gamma_A}{M_\infty} \sqrt{\frac{\bar{W}_\infty T_W}{2\pi \bar{\gamma}_\infty W_A T_\infty}} \quad (D30)$$

would yield the appropriate concentration slip for a fully catalytic surface.

With the following (somewhat inconsistent) assumptions, Eqs. (D23), (D25), (D27), and (D28) may be simplified to those obtained in refs. 8 and 11:

- (i) In pressure slip Eq. (D23),  $Pr = 1$  is employed along with approximations

$$\frac{4}{5} \left( \frac{\bar{\gamma}}{\bar{\gamma}-1} \right)_s \approx 3$$

and

$$\left( \frac{\bar{W}_S}{W_A} \right)^{3/2} \left[ C_A^S \bar{\mu}_A^S + \left( \frac{W_A}{W_M} \right)^{3/2} (1 - C_A^S) \bar{\mu}_M^S \right] \approx \bar{\mu}_S$$

- (ii) In velocity slip Eq. (D25) the following assumption is made for the mixture molecular weights

$$\frac{\bar{W}_\infty}{\bar{W}_S} \approx 1$$



- (iii) In temperature slip Eq. (D27) an assumption is made for the surface to be noncatalytic so that  $\bar{k}_{wA} = 0$ . In addition, Prandtl number (Pr) is taken unity and it is assumed that

$$\frac{1}{2} \left( \frac{\bar{\gamma}}{\bar{\gamma}-1} \right)_s = \frac{15}{8}$$

- (iv) No assumption is required in the concentration slip Eq. (D28). But it may not be appropriate to employ (Ref. 11) this equation for all the species of a multicomponent mixture. This equation is applicable to concentration slip of recombining atoms only in a binary (two-species) mixture (Ref. 8) of atoms and molecules.

No equation has been obtained in reference 8 or 11 to correspond to Eq. (D22) to obtain wall values of the species concentration ( $C_A^w$ ) from the values at the edge of the Knudsen layer ( $C_A^s$ ).

#### Slip Expressions For A Single Species Mixture

For a single species mixture ( $\gamma_A = 0$ ), the following slip expressions are obtained:

##### Density Slip

$$\frac{\bar{\rho}_s}{\bar{\rho}_w} = \sqrt{\frac{\bar{T}_w}{\bar{T}_s}} \quad (D31)$$

Pressure Slip

$$\bar{p}^S = \bar{p}^W + \frac{4}{5\sqrt{2\pi}} \left( \frac{\bar{\gamma}}{\bar{\gamma}-1} \right)_s \left( \frac{2-\theta}{\theta} \right) \frac{\epsilon^2}{Pr_s} \frac{\bar{\mu}_s}{\bar{T}_s} \sqrt{\frac{\bar{p}_s}{\bar{\rho}_s}} \left( \frac{\partial \bar{T}}{\partial \bar{n}} \right)_s \quad (D32)$$

Velocity Slip

$$\bar{u}^S = \sqrt{\frac{\pi}{2}} \left( \frac{2-\theta}{\theta} \right) \epsilon^2 \frac{\bar{\mu}_s}{\sqrt{\bar{p}_s \bar{\rho}_s}} \left( \frac{\partial \bar{u}}{\partial \bar{n}} - \frac{\bar{\kappa} \bar{u}}{1+\bar{n} \bar{\kappa}} \right) \quad (D33)$$

Temperature Slip [For a gas consisting of molecules only (i.e. diatomic perfect gas)]

$$\bar{T}_s = \bar{T}_w + \frac{1}{4} \sqrt{\frac{\pi}{2}} \left( \frac{\bar{\gamma}}{\bar{\gamma}-1} \right)_s \left( \frac{2-\theta}{\theta} \right) \frac{\epsilon^2}{Pr_s} \frac{\bar{\mu}_s}{\sqrt{\bar{p}_s \bar{\rho}_s}} \left( \frac{\partial \bar{T}}{\partial \bar{n}} \right)_s \quad (D34)$$

where we have used  $x_1 = \frac{1}{2}$ , or with frozen internal energy during reflection from the surface,

$$\bar{T}_s = \bar{T}_w + \frac{1}{2} \sqrt{\frac{\pi}{2}} \left( \frac{\bar{\gamma}}{\bar{\gamma}-1} \right)_s \left( \frac{2-\theta}{\theta} \right) \frac{\epsilon^2}{Pr_s} \frac{\bar{\mu}_s}{\sqrt{\bar{p}_s \bar{\rho}_s}} \left( \frac{\partial \bar{T}}{\partial \bar{n}} \right)_s \quad (D35)$$

Equations (D32) (D33) and (D35) are the ones employed in References 8 and 11 with  $Pr = 1$ .

### No-Slip Species Concentration Boundary Condition

#### Multicomponent Mixture

The no-slip boundary condition may be obtained from Eqs. (D17) and (D18). in the absence of slip, the Knudsen layer thickness shrinks to almost zero, the values at the top of the Knudsen layer become the wall

values (See Fig. 1):

$$C_i^w = 1 + \frac{\left\{ \frac{\partial C_i}{\partial \bar{n}} + \frac{W_A}{W_i} \bar{\psi}_i \right\}_w}{\sum_{q=1}^{NS} \left( \frac{\bar{W}}{W_q} \frac{\partial C_q}{\partial \bar{n}} \right)_w} ; \quad \begin{cases} A = 0 \text{ for } i = O_2; \\ A = N \text{ for } i = N_2; \end{cases} \quad (D36)$$

where

$$\bar{\psi}_A^w = - \left( \frac{2\gamma_A}{2-\gamma_A} \right) \left( \frac{1}{\epsilon^2 M_\infty} \right) \sqrt{\frac{\bar{W}_\infty T_w}{2\pi \bar{\gamma}_\infty W_A T_\infty}} \left( \frac{\bar{W}_w}{W_A} \right) \left( \frac{Pr}{Le} \right)_w \left( \frac{\bar{p}}{\mu} \right)_w C_A^w ;$$

$$A = O, N \quad (D37a)$$

$$\bar{\psi}_M^w = - \bar{\psi}_A^w ; \quad \begin{cases} A = 0 \text{ for } M = O_2 \\ A = N \text{ for } M = N_2 \end{cases} \quad (D37b)$$

$$\bar{\psi}_i = 0 \text{ for all other species} \quad (D37c)$$

where we have neglected the higher order shear (i.e.  $Py/p^w \approx 1$ ).

For the recombining O and N atoms, Eq. (D17) may also be written as

$$C_A^w = \left\{ \frac{\partial C_A}{\partial \bar{n}} + \sum_{q=1}^{NS} \left( \frac{\bar{W}}{W_q} \frac{\partial C_q}{\partial \bar{n}} \right) \right\}_w$$

$$/ \left\{ \sum_{q=1}^{NS} \left( \frac{\bar{W}}{W_q} \frac{\partial C_q}{\partial \bar{n}} \right)_w + \left( \frac{\bar{k}_{WA}}{\epsilon^2} \right) \left( \frac{\bar{W}_w}{W_A} \right) \left( \frac{Pr}{Le} \right)_w \left( \frac{\bar{p}}{\mu} \right)_w \right\} \quad (D38)$$

The recombination rate constant  $\bar{k}_{WA}$  in Eq. (D37a) and (D38) has been defined as (Ref. 2)

$$\bar{k}_{wA} = \left( \frac{2\gamma_A}{2-\gamma_A} \right) \frac{1}{M_\infty} \sqrt{\frac{\bar{W}_\infty T_w}{2\pi \bar{\gamma}_\infty \bar{W}_A T_\infty}} \quad (D39)$$

without slip and higher order shear.

For a noncatalytic wall (with  $\gamma_A = \bar{k}_{wA} = 0$ ), Eq. (D21) gives

$$\left( \frac{\partial C_i}{\partial \bar{n}} \right)_w = 0 \quad (D40)$$

for all the species of a multicomponent mixture with the binary assumption about the diffusion coefficients.

#### Binary Mixture

For a two-species mixture of atoms and molecules, Eq. (D28) gives

$$C_A^w = \frac{\epsilon^2}{\bar{k}_{wA}} \left( \frac{Le}{Pr} \right)_w \left( \frac{\bar{\mu}}{\bar{\rho}} \right)_w \left( \frac{\partial C_A}{\partial \bar{n}} \right)_w \quad (D41a)$$

which may also be obtained from Eq. (D38) for a surface with finite catalycity.  $\bar{k}_{wA}$  in Eq. (41a) is again obtained from Eq. (D39). For a noncatalytic surface with  $\bar{k}_{wA} = 0$ , Eq. (D41) gives

$$\left( \frac{\partial C_A}{\partial \bar{n}} \right)_w = 0 \quad (D42)$$

Eqs. (D41) and (D42) are obtained in ref. 4. However, ref. 4 employed Eq. (D30) in place of Eq. (D39) for obtaining the reaction rate constant,  $\bar{k}_{WA}$ . As obtained in ref. 2, Eq. (D30) is more appropriate when slip and higher order shear are included in the flowfield analysis (e.g. under rarefied or low density conditions).

If  $\bar{k}_{WA}$  is substituted from Eq. (D39) in Eq. (D41a), we may also obtain

$$C_A^W = \epsilon^2 \left( \frac{2-\gamma_A}{\gamma_A} \right) \left( \frac{Le}{Pr} \right)_W \sqrt{\frac{\pi \bar{W}_A}{2 \bar{W}_W}} \frac{\bar{\mu}_W}{\bar{p}_W} \sqrt{\frac{\bar{p}_W}{\bar{\rho}_W}} \left( \frac{\partial C_A}{\partial \bar{n}} \right)_W \quad (D41b)$$

where we have used the equation of state

$$\frac{\bar{p}_W}{\bar{\rho}_W} = \frac{1}{M_\infty^2} \left( \frac{T_W}{\bar{\gamma}_\infty T_\infty} \right) \frac{\bar{W}_\infty}{\bar{W}_W} \quad (D43)$$

Eq. (D41b) compares with the corresponding equation of ref. 8, if one keeps in mind that the diffusion coefficient  $F_D$  (of Ref. 8) in the absence of slip is related to the present variables by the relation

$$F_D^W = \bar{\mu}_W \left( \frac{Le}{Pr} \right)_W$$

It may be seen from Eqs. (41a) or (41b) that the gradient  $(\partial C_A / \partial \bar{n})_W$  is governed by the ratio  $\bar{k}_{WA} / \epsilon^2$  or  $\gamma_A / \epsilon^2$ . Therefore, for surfaces which are almost noncatalytic, this ratio would be of the order of one for large values of the Reynolds number parameter  $(1/\epsilon^2)$ . This would imply that a

surface may behave effectively as more catalytic under high density than under low density conditions.

## APPENDIX E

### SLIP CONDITIONS IN THE SPHERICAL COORDINATES

For analyzing the flow in the stagnation region of a body, it is convenient to use the spherical polar coordinates  $(r, \phi)$  for the two-dimensional flow. The following relations exist between the spherical polar and the body-oriented  $(s^*, n^*)$  coordinates over the spherical portion of a body

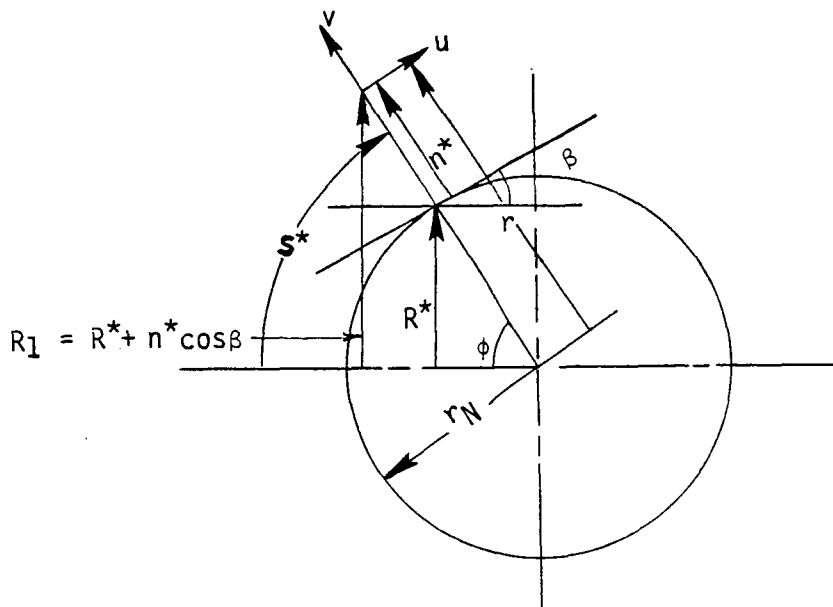


Figure E1. Coordinate Configuration

$$\left. \begin{aligned} r \sin \phi &= R^* + n^* \cos \beta \\ r &= r_N + n^* = r_N (1 + n^* \kappa) \quad ; \quad \kappa = \frac{1}{r_N} \\ r_N \phi &= s^* \quad ; \quad B = 90 - \phi \end{aligned} \right\} \quad (E1)$$

or, in the non-dimensional form,

$$\left. \begin{aligned} \bar{r} \sin \phi &= \bar{R} + \bar{n} \cos \phi \\ \bar{r} &= \bar{r}_N + \bar{n} = 1 + \bar{n} \quad ; \quad \bar{\kappa} = 1 \\ \phi &= \bar{s} \quad ; \quad \partial \bar{r} = \partial \bar{n} \quad ; \quad \partial \phi = \partial \bar{s} \end{aligned} \right\} \quad (E2)$$

where we have used nose radius,  $r_N$ , to nondimensionalize all the distances (see Appendix D).

Using the relations given by (E2) in Eqs. (D11) through (D19), we can obtain the slip equations in the spherical polar coordinates for a multicomponent mixture. Once again, these equations employ the simplifications given for a multicomponent mixture, following Eq. (38c) of the main text.

Concentration Slip

$$\frac{C_i^S}{C_i^W} = 2 \left( \frac{\bar{\rho}_W}{\bar{\rho}_S} \right) \left[ 1 + \frac{1}{2} M_\infty \bar{M}_{iy} \sqrt{2\pi \bar{\gamma}_\infty \left( \frac{\bar{W}_i}{\bar{W}_\infty} \right) \left( \frac{\bar{T}_\infty}{\bar{T}_W} \right)} \right] \sqrt{\frac{\bar{T}_W}{\bar{T}_S}} \\ / \left( \frac{\bar{p}_y}{\bar{p}^S} + 1 \right) \quad (E3)$$

where

$$\bar{M}_{Ay} = -\bar{k}_{wA} \quad ; \quad A = 0, N \quad (E4a)$$



$$\bar{M}_{My} = \bar{k}_{WA} \left( \frac{C_A}{C_M} \right)_w ; \begin{cases} A = O \text{ for } M = O_2; \\ A = N \text{ for } M = N_2; \end{cases} \quad (E4b)$$

$$\bar{M}_{iy} = 0 \quad \text{for all other atoms and molecules} \quad (E4c)$$

Pressure Slip

$$\begin{aligned} \bar{p}^s = & \left\{ \bar{p}_w - \epsilon^2 \left[ \frac{2}{3} \bar{\mu} \left( \frac{1}{\bar{r}} \frac{\partial \bar{u}}{\partial \phi} - 2 \frac{\partial \bar{v}}{\partial \bar{r}} \right) \right]_s \right. \\ & + \epsilon^2 \left[ \frac{2}{5\sqrt{\pi}} \left( \frac{2-\theta}{\theta} \right) \left( \frac{\bar{\gamma}}{\bar{\gamma}-1} \right)_s \left( \frac{1}{M_\infty Pr_s} \right) \sqrt{\frac{2 T_{ref} \bar{T}_s \bar{W}_\infty}{\bar{\gamma}_\infty T_\infty W_s}} \left( \frac{1}{\bar{T}} \frac{\partial \bar{T}}{\partial \bar{r}} \right)_s \right. \\ & \times \sum_{i=1}^{NS} \left( \frac{\bar{W}_s}{W_i} \right)^{3/2} C_i^s \bar{\mu}_i^s \left. \right\} / \left\{ 1 - \frac{4}{\sqrt{\pi}} \left( \frac{2-\theta}{\theta} \right) \epsilon^2 \left( \frac{Le_s M_\infty}{Pr_s} \right) \sqrt{\frac{\bar{\gamma}_\infty T_\infty}{2 T_{ref} \bar{T}_s}} \left( \frac{\bar{\mu}_s}{\rho_s} \right) \right. \\ & \times \sum_{i=1}^{NS} \sqrt{\frac{W_i}{\bar{W}_\infty}} \left[ \frac{\partial C_i}{\partial \bar{r}} + (1-C_i) \sum_{q=1}^{NS} \left( \frac{\bar{W}}{W_q} \right) \frac{\partial C_q}{\partial \bar{r}} \right]_s \left. \right\} \quad (E5) \end{aligned}$$

Velocity Slip

$$\begin{aligned} \bar{u}^s = & \epsilon^2 \left( \frac{M_\infty \bar{\mu}_s}{\rho_s} \right) \left( \frac{1}{\sum_{i=1}^{NS} \sqrt{\frac{\bar{W}}{W_i}} C_i} \right)_s \left[ \sqrt{\pi} \left( \frac{2-\theta}{\theta} \right) \sqrt{\frac{\bar{\gamma}_\infty T_\infty}{2 T_{ref} \bar{T}_s}} \left( \frac{\partial \bar{u}}{\partial \bar{r}} - \frac{\bar{u}}{\bar{r}} \right) \right. \\ & + \frac{1}{\bar{r}} \frac{\partial \bar{v}}{\partial \phi} \left. \right]_s + \frac{1}{5} \frac{1}{M_\infty Pr_s} \left( \frac{\bar{\gamma}}{\bar{\gamma}-1} \right)_s \left( \frac{1}{\bar{T}} \frac{\partial \bar{T}}{\partial \phi} \right)_s \sum_{i=1}^{NS} \left( \frac{\bar{W}_s}{W_i} \right)^{3/2} C_i^s \frac{\bar{\mu}_i^s}{\bar{\mu}_s} \end{aligned}$$

$$+ \frac{Le_s}{M_\infty Pr_s} \sum_{i=1}^{NS} \sqrt{\frac{W_i}{\bar{W}_s}} \left\{ \frac{1}{r} \frac{\partial C_i}{\partial \phi} + (1-C_i) \sum_{q=1}^{NS} \left( \frac{W}{W_q} \frac{\partial C_q}{r \partial \phi} \right) \right\}_s \quad (E6)$$

Temperature Slip

$$\begin{aligned} \frac{\bar{T}_s}{\bar{T}_w} = & \left\{ -\sqrt{\frac{\pi}{2}} \left( \frac{\bar{p}_w}{\sqrt{\bar{p}_s \bar{\rho}_s}} \right) \left[ \sum_{i=1}^{NS} M_{i,y} C_i^w \left( \frac{\bar{W}_s}{W_i} \right) + \sum_i M_{i,y} C_i^w \left( \frac{\bar{W}_s}{W_i} \right) \right] \right. \\ & \text{diatomic molecules} \\ & + \frac{1}{2} \left( \frac{p_y}{p^s} + 1 \right) \left[ \sum_{i=1}^{NS} \left( \frac{\bar{W}_s}{W_i} \right)^{3/2} C_i^s + \sum_i \left( \frac{\bar{W}_s}{W_i} \right)^{3/2} C_i^s \right] \Big\} \\ & \text{diatomic molecules} \\ & / \left[ -\sqrt{\frac{\pi}{2}} \left( \frac{2-\theta}{\theta} \right) \left\{ \frac{\epsilon^2}{2\gamma_\infty} \left( \frac{1}{M_\infty^2 Pr_s} \right) \left( \frac{\bar{u}}{\bar{p}} \right)_s \left( \frac{\bar{y}}{\bar{y}-1} \right)_s \left( \frac{T_{ref}}{T_\infty} \right) \sqrt{\frac{\bar{p}_s}{\bar{p}_s}} \right. \right. \\ & \times \left( \frac{W_\infty}{W_s} \right) \left( \frac{\partial \bar{T}}{\partial r} \right)_s - \frac{5}{4} \left( \frac{\bar{p}_w}{\sqrt{\bar{p}_s \bar{\rho}_s}} \right) \sum_{i=1}^{NS} M_{i,y} C_i^w \left( \frac{\bar{W}_s}{W_i} \right) \\ & - \left( \frac{\bar{p}_w}{\sqrt{\bar{p}_s \bar{\rho}_s}} \right) \sum_i M_{i,y} C_i^w \left( \frac{\bar{W}_s}{W_i} \right) \Big\} + \frac{1}{4} \left( 3 \frac{p_y}{p^s} + 1 \right) \sum_{i=1}^{NS} \left( \frac{\bar{W}_s}{W_i} \right)^{3/2} C_i^s \\ & \text{diatomic molecules} \\ & + \frac{1}{2} \left( \frac{p_y}{p^s} + 1 \right) \sum_i \left( \frac{W_s}{W_i} \right)^{3/2} C_i^s \Big] \quad (E7) \\ & \text{diatomic molecules} \end{aligned}$$

or, with frozen internal energy during reflection from surface,

$$\frac{\bar{T}_s}{\bar{T}_w} = \left\{ -\sqrt{\frac{\pi}{2}} \left( \frac{\bar{\rho}_w}{\sqrt{\bar{p}_s \bar{\rho}_s}} \right) \sum_{i=1}^{NS} \bar{M}_{iy} C_i^w \left( \frac{\bar{W}_s}{W_i} \right) + \frac{1}{2} \left( \frac{p_y}{p^s} + 1 \right) \sum_{i=1}^{NS} \left( \frac{\bar{W}_s}{W_i} \right)^{3/2} C_i^s \right.$$

$$\left. / \left[ -\sqrt{\frac{\pi}{2}} \left( \frac{2-\theta}{\theta} \right) \left\{ \frac{\epsilon^2}{2\gamma_\infty} \left( \frac{1}{M_\infty^2 Pr_s} \right) \left( \frac{\bar{\mu}}{\bar{p}} \right)_s \left( \frac{\bar{\gamma}}{\bar{\gamma}-1} \right)_s \left( \frac{T_{ref}}{T_\infty} \right) \sqrt{\frac{\bar{\rho}_s}{\bar{p}_s}} \right. \right. \right.$$

$$\left. \times \left( \frac{W_\infty}{W_s} \right) \left( \frac{\partial \bar{T}}{\partial r} \right)_s - \frac{5}{4} \left( \frac{\bar{\rho}_s}{\sqrt{\bar{p}_s \bar{\rho}_s}} \right) \sum_{i=1}^{NS} \bar{M}_{iy} C_i^w \left( \frac{\bar{W}_s}{W_i} \right) \right\}$$

$$\left. + \frac{1}{4} \left( 3 \frac{p_y}{p^s} + 1 \right) \sum_{i=1}^{NS} \left( \frac{\bar{W}_s}{W_i} \right)^{3/2} C_i^s \right] \quad (E8)$$

$$C_i^s = 1 + \frac{\left\{ \frac{\partial C_i}{\partial r} + \frac{W_A}{W_i} \bar{\psi}_i \right\}_s}{\sum_{q=1}^{NS} \left( \frac{W}{W_q} \frac{\partial C_q}{\partial r} \right)_s} ; \quad \begin{cases} A = 0 \text{ for } i = O_2; \\ A = N \text{ for } i = N_2; \end{cases} \quad (E9)$$

where

$$\bar{\psi}_A^s = - \frac{\gamma_A}{(2-\gamma_A)} \left( \frac{1}{\epsilon^2 M_\infty} \right) \sqrt{\frac{\bar{W}_\infty T_s}{2\pi \bar{\gamma}_\infty W_A T_\infty}} \left( \frac{\bar{W}_s}{W_A} \right) \left( \frac{Pr}{Le} \right)_s \left( \frac{\bar{\rho}}{\bar{\mu}} \right)_s \left( \frac{p_y}{p^s} + 1 \right) C_A^s ;$$

$$A = O, N \quad (E10a)$$

$$\bar{\psi}_M^s = -\bar{\psi}_A^s ; \begin{cases} A = O \text{ for } M = O_2 \\ A = N \text{ for } M = N_2 \end{cases} \quad (E10b)$$

$$\bar{\psi}_i^s = 0 \text{ for all other species} \quad (E10c)$$

and

$$\begin{aligned} \frac{p_y}{p^s} = \frac{\bar{p}_y}{\bar{p}_s} &= \left[ 1 + \frac{2}{3} \left( \frac{\bar{Y}_\infty T_\infty}{T_{ref}} \right) \left( \frac{\bar{\mu}}{\bar{\rho} \bar{T}} \right)_s \left( \frac{\bar{W}_s}{\bar{W}_\infty} \right) \epsilon^2 M_\infty^2 \right. \\ &\quad \left. \times \left( \frac{\partial \bar{u}}{r \partial \phi} - 2 \frac{\partial \bar{v}}{\partial r} \right)_s \right] \end{aligned} \quad (E11)$$

In obtaining these various equations, the following form of the equation of state has been employed:

$$\frac{\bar{p}_s}{p^s} = \frac{1}{M_\infty^2} \left( \frac{\bar{T}_s T_{ref}}{\bar{Y}_\infty T_\infty} \right) \left( \frac{\bar{W}_\infty}{\bar{W}_s} \right) \quad (E12)$$

Similar to Appendix D, Eqs. (E3) through (E11) may further be simplified for a binary mixture and for a single species mixture.

## APPENDIX F

### INTEGRALS REQUIRED FOR OBTAINING VARIOUS FLUXES

In order to obtain the normal fluxes of mass, momentum, and energy, it is necessary to evaluate various integrals over the velocity space of the distribution function. These integrals involve terms that are various velocity moments of the distribution function. The integrals are provided for the net, incident, and specularly reflected fluxes. These integrals are basically the same as those provided in Reference 2 except for some corrections and additions.

#### F1. Integrals Over the Entire Velocity Space (For Net Quantities)

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y e^{-W^2} d^3 W = 0$$

$$\begin{aligned} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y W_i e^{-W^2} d^3 W &= 0 & i \neq y \\ &= \frac{1}{2} \pi^{3/2} & i = y \end{aligned}$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y W^2 e^{-W^2} d^3 W = 0$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y W_i W_j e^{-W^2} d^3 W = 0$$

$$\begin{aligned} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y W_i W^2 e^{-W^2} d^3 W &= 0 & i \neq y \\ &= \frac{5}{4} \pi^{3/2} & i = y \end{aligned}$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y^2 W_i^2 e^{-W^2} d^3 W = \frac{1}{4} \pi^{3/2} \quad i \neq y$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y^2 W_i W_j e^{-W^2} d^3 W = 0 \quad i \neq j$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y^4 e^{-W^2} d^3 W = \frac{3}{4} \pi^{3/2}$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y^2 W_i W_j^2 e^{-W^2} d^3 W = 0$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y^2 W_i W^2 e^{-W^2} d^3 W = 0$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y W_i W_j W^2 e^{-W^2} d^3 W = 0$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y W^4 e^{-W^2} d^3 W = 0$$

$$\begin{aligned} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y W_i W^4 e^{-W^2} d^3 W &= 0 \quad i \neq y \\ &= \frac{35}{8} \pi^{3/2} \quad i = y \end{aligned}$$

F2. Integrals Over the Lower Half Velocity Space (For Incident Quantities)

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y e^{-W^2} d^3 W = -\frac{\pi}{2}$$

$$\begin{aligned} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y W_i e^{-W^2} d^3 W &= 0 \quad i \neq y \\ &= \frac{1}{4} \pi^{3/2} \quad i = y \end{aligned}$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^0 \int_{-\infty}^{\infty} W_y W^2 e^{-W^2} d^3 W = -\pi$$

$$\begin{aligned} \int_{-\infty}^{\infty} \int_{-\infty}^0 \int_{-\infty}^{\infty} W_y W_i W_j e^{-W^2} d^3 W &= 0 & i \neq j \\ &= -\frac{\pi}{4} & i = j \neq y \\ &= -\frac{\pi}{2} & i = j = y \end{aligned}$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^0 \int_{-\infty}^{\infty} W_y W_{||} W_i W_j e^{-W^2} d^3 W = 0 \quad \begin{aligned} &i \neq j \text{ and} \\ &i \text{ or } j \neq || \end{aligned}$$

$$\begin{aligned} \int_{-\infty}^{\infty} \int_{-\infty}^0 \int_{-\infty}^{\infty} W_y W_i W^2 e^{-W^2} d^3 W &= 0 & i \neq y \\ &= \frac{5}{8} \pi^{3/2} & i = y \end{aligned}$$

$$\begin{aligned} \int_{-\infty}^{\infty} \int_{-\infty}^0 \int_{-\infty}^{\infty} W_y^2 W_i W_j e^{-W^2} d^3 W &= 0 & i \neq j, i \text{ or } j \neq y \\ &= \frac{1}{8} \pi^{3/2} & i = j \neq y \\ &= \frac{3}{8} \pi^{3/2} & i = j = y \end{aligned}$$

$$\begin{aligned} \int_{-\infty}^{\infty} \int_{-\infty}^0 \int_{-\infty}^{\infty} W_y^2 W_i W^2 e^{-W^2} d^3 W &= 0 & i \neq y \\ &= -\frac{3}{2} \pi & i = y \end{aligned}$$

$$\begin{aligned} \int_{-\infty}^{\infty} \int_{-\infty}^0 \int_{-\infty}^{\infty} W_y W_{||} W_i W^2 e^{-W^2} d^3 W &= 0 & i \neq || \neq y \\ &= -\frac{3\pi}{4} & i = || \neq y \end{aligned}$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^0 \int_{-\infty}^{\infty} W_y W^4 e^{-W^2} d^3 W = -3\pi$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} W_y W_i W^4 e^{-W^2} d^3 W = 0 \quad i \neq y$$

$$= \frac{35}{16} \pi^{3/2} \quad i = y$$

F3. Integrals Over the Upper Half Velocity Space (For Specularly Reflected Quantities)

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y e^{-W^2} d^3 W = \frac{\pi}{2}$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y W_i e^{-W^2} d^3 W = 0 \quad i \neq y$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y (-W_y) e^{-W^2} d^3 W = -\frac{1}{4} \pi^{3/2}$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y W^2 e^{-W^2} d^3 W = \pi$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y W_i W_j e^{-W^2} d^3 W = 0 \quad i \neq j$$

$$= \frac{\pi}{4} \quad i = j \neq y$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y (-W_y)^2 e^{-W^2} d^3 W = \frac{\pi}{2}$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y W_{||} W_i W_j e^{-W^2} d^3 W = 0 \quad i \neq j \text{ and}$$

$$i \text{ or } j \neq ||$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y W_i W^2 e^{-W^2} d^3 W = 0$$



$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y (-W_y) W^2 e^{-W^2} d^3 W = -\frac{5}{8} \pi^{3/2}$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y^2 W_i W_j e^{-W^2} d^3 W = 0 \quad i \neq j, i \text{ or } j \neq y$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y (-W_y) W_i^2 e^{-W^2} d^3 W = -\frac{1}{8} \pi^{3/2} \quad i \neq y$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y^2 (-W_y)^2 e^{-W^2} d^3 W = \frac{3}{8} \pi^{3/2}$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y^2 W_i W^2 e^{-W^2} d^3 W = 0 \quad i \neq y$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y (-W_y)^2 W^2 e^{-W^2} d^3 W = \frac{3\pi}{2}$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y W_{||} W_i W^2 e^{-W^2} d^3 W = 0 \quad i \neq || \neq y$$

$$= \frac{3\pi}{4} \quad i = || \neq y$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y W^4 e^{-W^2} d^3 W = 3\pi$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y W_i W^4 e^{-W^2} d^3 W = 0 \quad i \neq y$$

$$\int_{-\infty}^{\infty} \int_0^{\infty} \int_{-\infty}^{\infty} W_y (-W_y) W^4 e^{-W^2} d^3 W = -\frac{35}{16} \pi^{3/2}$$

$(-W_y)$  appearing in the integrals emphasizes that the sign of the thermal velocity component normal to the surface,  $V_y$  (and consequently that of  $W_y$ ) changes in the distribution function  $f_s^\dagger$  upon reflection from the surface.

END

DATE

NOV. 5, 1987